ANDREWS, MARY ANNA. Binary Nematic Mixtures of 4,4'-Dialkoxyazoxybenzene Homologs. (1970) Directed by: Dr. J. P. Schroeder. pp. 86

Four phase diagrams of binary mixtures of nematogenic dialkoxyazoxybenzenes were constructed by determining the melting range and nematic-isotropic (N-I) transition range of various compositions of the binary systems. The components included 4,4'-dimethoxy- (1a), 4,4'-diethoxy- (1b), 4,4'-di-n-butyloxy- (1c) and 4,4'-di-n-hexyloxyazoxybenzene (1d). All mixtures give nematic mesophases in which the molecular order is intermediate relative to the nematic mesophase of the pure components. The eutectic mixtures generally exhibit the widest nematic range. The noneutectic mixtures having N-I transition temperatures higher than the corresponding eutectic mixture often exhibit nematic ranges greater than the eutectic mixture due to their ability to be supercooled.

Binary mixtures from these systems and also pure 1c were used as stationary liquid phases in gas-liquid partition chromatography (glpc) to determine the selectivity of their nematic mesophases toward the positional isomers m- and p-xylene. This selectivity is an indication of the molecular order within the mesophase. The molecular order of the pure compounds was found to be in the same order as that of their N-I transition temperatures. The results from the mixtures, however, demonstrate that the N-I transition temperature is only a rough indication of order.

The maximum selectivity of a mesophase is reached at the lowest temperature that is attainable without crystallization. Most of the phases studied can be classified as highly selective and several are exceptionally so. The compounds in decreasing order of maximum selectivity are 1b, 1c, 1d and 1a. The order in which the pure components contribute to the selectivities of a mixture are also 1b > 1c > 1d > 1a. That is, 1b mixtures are more selective than 1c mixtures, etc. Also selectivity increases with increasing concentration of the more selective of the components. Nematic mixtures of 1 homologs are most selective when the components are highly selective and have alkyl groups of comparable length. The performance is also excellent if one component is highly selective and present in high concentration. This is reasonable in that one would expect a selective homolog to have a strong molecular ordering effect in a mixed nematic mesophase, and minimum disruption of a mixed mesophase when the components are structurally similar.

From a practical standpoint, the high selectivity of the nematic mixtures is significant because it gives promise of broadening the usefulness of nematic solvents as stationary liquid phases in glpc. By varying the components and compositions of mixtures, operating temperature ranges can be changed and controlled without sacrificing performance and, in some instances, with improved performance. By contrast, the

smaller number and fixed nematic ranges of pure compounds are severe limitations.

BINARY NEMATIC MIXTURES OF 4,4'-DIALKOXYAZOXYBENZENE HOMOLOGS

by

Mary A. Andrews

A Thesis Submitted to
the Faculty of the Graduate School of
The University of North Carolina at Greensboro
in Partial Fulfillment
of the Requirements for the Degree
Master of Science

Greensboro
October, 1970

Approved by

J. P. Schroeder
Thesis Adviser

APPROVAL SHEET

This thesis has been approved by the following committee of the Faculty of the Graduate School at The University of North Carolina at Greensboro.

Thesis Adviser J. P. Schroeder

Oral Examination Committee Members J. P. Schroeder

Walter H. Peterborgh

C. H. Wanselow

W. K. Bates

October 8, 1970
Date of Examination

ACKNOWLEDGMENT

For his suggestions, guidance, and encouragement in the research work and his time and consideration given during the completion of this thesis, the author wishes to express her appreciation to Dr. J. P. Schroeder. For her aid in experimental work the author would like to express her thanks to Dr. D. C. Schroeder. The author would like to express her appreciation to the staff of the Chemistry Department of The University of North Carolina at Greensboro whose encouragement and stimulus to scholarship have contributed greatly to this study.

The author also wishes to acknowledge the research grant from The University of North Carolina at Greensboro which supported this study.

M. A. A.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Figure | Page

INTRODUCTION

Liquid Crystals

The term liquid crystal is applied to a compound which melts to an anisotropic, birefringent liquid. The term mesophase was used by Friedel[1] for this state of matter to stress that it is intermediate between crystalline solid and isotropic liquid. Similarly, liquid crystallinity is often called mesomorphism. Friedel carried out detailed optical studies[1] that enabled him to distinguish three different types of mesophases, two of which - nematic and smectic - are pertinent to this study. The nematic mesophase is a turbid, highly fluid liquid when the sample is melted in a capillary tube, and can be distinguished from the more viscous smectic mesophase, which adheres to the walls of the tube.[2]

A more exact method of distinguishing these two states is possible because of the characteristic textures[2] observable when a sample of the liquid crystal is mounted as a film between a glass slide and cover slip, and viewed between crossed polarizing filters under a microscope. The nematic texture most often obtained is the threaded texture. As the isotropic liquid is cooled, spherical birefringent droplets appear which exhibit a dark cross of extinction. As these coalesce, numerous fine dark lines or threads are observed.

The most common texture of the smectic mesophase is the focal-conic texture. When the isotropic liquid is cooled,

the mesophase separates from the isotropic melt in somewhat elongated, irregular-shaped, birefringent bodies described by Friedel[2] as "batonnets". As the temperature falls, these coalesce into larger batonnets which finally fill the entire field of view, and the focal-conic texture of the smectic mesophase is produced. When the mesophase is observed by means of a microscope, it is seen to be quite immobile, unlike the nematic mesophase. By casual observation, this texture can readily be confused with a crystalline solid. The illusion is dispelled when it is found that a displacement of the cover slip may be made quite easily. When the focal-conic groups are large, the preparation contains an arrangement of fine dark lines.

A parallel molecular arrangement is required to give mesophases. The smectic mesophase also has a layered arrangement of the parallel molecules, with their ends in line. These strata may be flat or highly distorted in a bulk sample. The arrangement appears to extend continuously from one surface to another for fairly thin sections.

The nematic mesophase also consists of molecules which are parallel to one another, but with no regular arrangement about the ends of the molecules. The parallel alignment persists only in groups of some 100,000 molecules. These are referred to as swarms (the Swarm Theory, first proposed by E. Bose[3] in 1909).

Nematic compounds typically have long, rod-shaped molecules with dipolar groups, which may be either centrally or terminally located. Because of the elongated molecular shape and the attractive forces between neighboring dipolar molecules, there is a tendency for the molecules to arrange themselves parallel to one another. Ornstein and Kast[4] proposed that the swarm itself is elongated, its major axis coinciding with the major axis of the elongated molecules. For a given system, the size of the swarms should be more or less constant, but the uniform direction of the major molecular axis within a swarm does not extend throughout the medium. In the region between the swarms, the molecules are arranged in such a way that their orientation gradually changes from that of one swarm to that of the next. The swarm size will depend to some extent on the temperature of the mesophase, since the thermal agitation due to increased temperature will cause molecules to break away from the swarm. The molecular units in the swarm should not be considered as remaining in that swarm alone, but should be regarded as continually and rapidly exchanging with the molecules in other swarms and in intermediate regions of the mesophase.

As the temperature of the nematic mesophase is increased, the thermal agitation of the molecules increases and thus the size of the swarms decreases. Also, the parallel order of the molecules within the swarm decreases as the lateral

intermolecular forces are weakened. At a precise temperature these intermolecular forces weaken to such an extent that they are unable to maintain the parallel orientation against thermal movement of the molecules with rising temperature, and the nematic-isotropic liquid transition occurs. The sample, under crossed polaroids, exhibits an opaque front moving quickly across the field of view as the transition occurs. For pure liquid crystalline compounds the isotropic to nematic transition exhibits no supercooling, the nematic-isotropic (N-I) transition temperature being the same on heating and cooling. The molecular organization, which is disrupted very rapidly at the N-I transition, is restored with equal rapidity on cooling.

In a nematic mesophase, flow is accomplished by the molecules passing by one another while maintaining the parallel relationship and the viscosity is relatively low. In a smectic mesophase, however, flow can only be in the plane of the layers of molecules with one layer passing over another. At right angles to the smectic planes, the viscosity would be extremely high, since in this direction the system is equivalent to a section of crystalline material. In a small bulk of mesophase, however, the smectic layers will be highly distorted as the order is reminiscent of the three-dimensional ordering of the molecules in the crystal, and the anisotropic mesophase maintains in its texture

a pattern of discontinuities apparently identical with that of the crystalline areas. Therefore, an average, high viscosity will be obtained.

The tendency toward a parallel arrangement would seen to follow from compounds which possess the feature of molecular anisotropy - the molecules being elongated and rod-like in shape, rather than short and bulky. It is observed that the majority of mesomorphic compounds are geometrically anisotropic. Sufficient attractive forces must operate between the molecules to maintain a parallel arrangement after the crystal lattice has melted. Therefore, the long, narrow molecules must contain groups of atoms with which are associated permanent dipole moments, and the molecule itself must be highly polarizable.

Since in the smectic mesophase the layers of parallel molecules are free to move over one another, the intermolecular lateral attractions must be greater than the terminal attractions, maintaining the parallel arrangement while allowing flow. The probability that a smectic mesophase be exhibited by a compound, therefore, depends on the degree of difference between the terminal and lateral attractions.

The nematic mesophase may be formed directly upon melting of the crystalline solid, or it may be formed upon heating a smectic mesophase; the thermal vibrations eventually become great enough to overcome the strong primary lateral intermolecular attractions and the molecules are no longer able to maintain their layered arrangement. In a molecular

system which gives both smectic and nematic mesophases, the primary terminal cohesions between the ends of the molecules are overcome at the solid-smectic transition and the primary lateral forces at the smectic-nematic transition. The residual terminal and lateral attractions maintain the parallel arrangement in the nematic mesophase.

There are two possible types of molecular arrangements which, according to Gray[5], may give rise to a nematic melt directly from the solid. These may be envisaged as:

(1) A layer crystal lattice which becomes nematic by weakening of both the primary terminal and lateral attractions at the melting point. That is, the terminal and lateral attractions must be of roughly equal strength. If the lateral attractive forces are much greater than the terminal, a smectic mesophase is favored.

(2) An imbricated molecular arrangement in the crystal lattice, in which the parallel molecules are arranged in a regular manner with the ends of the molecules in a set pattern, though not with ends of adjacent molecules side-by-side. Here, the molecular configuration in the solid is essentially identical to that in a nematic mesophase so transition to the latter is highly favored.

In short, if a molecule is structurally suitable for mesomorphism, in the sense that it is long and narrow, and possesses polarizable aromatic rings or other groups, but possesses no very long alkyl chain and no strong dipole

moments operating across the long axis, then the compound is most likely to exhibit nematic properties.

Liquid Crystals as Stationary Liquid Phases

Liquid crystals have the ability to behave mechanically as liquids while preserving some of the order of crystalline solids. This unique combination of properties makes them interesting as solvents. Specifically, nematic and smectic liquid crystals have been found to be useful as stationary liquid phases in gas-liquid partition chromatography.[6-9]

Gas-liquid partition chromatography[10] (glpc) is a process by which a mixture is separated into its constituents by a moving gas phase passing over a nonvolatile liquid sorbent (stationary liquid phase) coated on an inert solid. The mobile phase or carrier gas is an inert gas which is made to flow at a constant rate through a column containing the sorbent.

When a sample of a mixture is injected into the gas stream, the components move through the column at different rates dependent on their respective volatilities and interactions with the nonvolatile liquid phase. The various molecules tend to dissolve and revaporize as they pass down the column, and the molecules of the component having the greater solubility in the liquid phase are retarded in their passage. With a liquid phase of suitable properties and a column of sufficient length, the partition process between the gas and liquid phases results in a situation in which each component

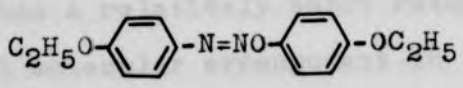
of the sample emerges in time from the end of the column as a binary mixture with the carrier gas.

The order of elution from a chromatographic column depends upon the relative volatilities of solutes which in turn are dependent on solute-solvent interaction forces such as polarity, chemical interaction, hydrogen bonding and other cohesive forces.

The order of elution will be according to boiling points when dispersion forces alone exist as the solution forces. However, when chemical adducts, induction forces, or orientation forces exist, the order of elution is not necessarily governed by boiling point. A stationary liquid phase is said to be selective if it causes compounds with identical boiling points to pass through a chromatographic column at substantially different rates[10] or if it reverses the order of elution relative to respective boiling points. Benzene, for example, (b.p., 80.1 °C) is retained longer on a polar liquid phase than cyclohexane (b.p., 80.8 °C). On a nonpolar liquid phase in which only London forces exist, the order of elution is reversed, the compounds being eluted in order of their boiling points.

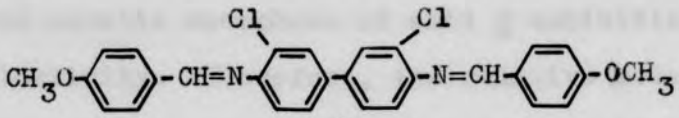
It has been shown[6-8] that nematic liquids exhibit a selective affinity toward linear, rod-shaped solute molecules relative to bulky, nonlinear molecules. Separation of m- and p-xylene by glpc has proved to be quite a problem. There is

only a slight difference in polarity of the molecules, and the boiling points of m- and p-xylene are 139.1 and 138.4 °C, respectively. Therefore, their retention times are nearly identical for most stationary liquid phases, the meta isomer being eluted last. When a m-, p-xylene mixture is passed over a nematic stationary phase, the linear p-xylene molecules (lower boiling) are invariable eluted last. As they dissolve in the parallel molecular arrangement of the liquid crystal, the more rod-shaped para molecules are oriented parallel to the molecules of the solvent. The increased solute-solvent attractive forces that result from this better "fit" hold back the para molecules. The more bulky meta molecules are held less strongly and are eluted sooner. This trend is further substantiated by glpc results[8] on the separation of meta-para isomer pairs of dichlorobenzene, methylanisole, ethyltoluene which also show the selective retention of the para isomer. The preference of nematic solvents for linear, rod-shaped molecules over bulky, nonlinear molecules is shown very vividly in the order of elution of methyl, ethyl, and isopropyl benzoates on stationary liquid phases of 4,4'-diethoxyazoxybenzene (1b) and 4,4'-bis(p-methoxyben-



1b

zylideneamino)-3,3'-dichlorobiphenyl (2).[8] In a silicone



2

column, the order of elution is methyl, ethyl, isopropyl ester with a large interval between the first two (relative retentions: 1.00, 1.64, 1.98) in agreement with the respective boiling points: 199°, 212°, 218.5 °C. The relative retentions for the methyl, ethyl and isopropyl esters on a 1b column are 1.00, 1.23 and 1.08, respectively, on a 2 column they are 1.00, 1.11 and 0.85. For the 1b column, the retention times of the methyl and ethyl benzoates are quite close together and the isopropyl ester is eluted well before the lower boiling ethyl ester. For 2, which has a better-ordered nematic mesophase, the "dislike" for the isopropyl ester is more spectacular, and it is eluted even before the methyl ester. Of these esters, methyl benzoate has the most linear molecule and, hence a long retention time in consideration of its boiling point. The isopropyl benzoate, with its bulky alkyl group, is unable to fit readily into the parallel arrangement of the nematic solvent and, therefore, has a relatively short retention time.[8]

The parallel molecular arrangement in the nematic mesophase effects a separation primarily on the basis of molecular geometry. The chromatographic results from 1b and 2 suggest that the efficiency, or the degree of separation,

of the columns is related to mesophase molecular order, the well-ordered nematic mesophase of anil 2 exhibiting a much greater selectivity. Therefore, the relative molecular orders of mesophases can be estimated from their efficiencies in separating a given meta-para isomer pair. A particularly sensitive test for regularity in the parallel molecular alignment of a mesophase is its ability to accomplish the difficult separation of m- and p-xylene. This, therefore, is the principal test used to measure the relative molecular orders in the systems studied in this work.

The primary criterion for molecular order and, hence, good selectivity of a nematic stationary phase is a high N-I transition temperature. This is desirable since it implies that the forces maintaining the ordered arrangement of molecules in the mesophase are relatively strong. In such a case, discrimination between solutes on the basis of molecular shape is relatively good.[6] If, in addition, the melting point is low, the situation is ideal because this provides a long useful temperature range and especially the opportunity to operate at low temperatures, where molecular order is even better. The lower limit of the nematic range is defined by either a nematic-solid transition (crystallization), or a nematic-smectic transition. These transitions are noted on a glpc chromatogram by a sharp drop in retention time, both the solid and smectic phases being poorer solvents than the nematic liquid.

Some years ago, Tolstoi[11], proposed that the parallel molecular order of a nematic mesophase is maintained to a certain extent above the usually assigned N-I transition temperature. The Swarm Theory proposes that aggregates of parallel molecules exist in the isotropic liquid which are too small to impose readily detectable anisotropic properties in the bulk of material. Retention of molecular order just above the N-I transition temperature is confirmed by glpc relative retention (α) values greater than 1.00 for p-xylene (m-xylene = 1.00). On cooling, there is a rapid increase in α at the transition point as the nematic "lattice" forms and discriminates strongly between m- and p-xylene. Below the transition point, α continues to ascend with decreasing temperature, reflecting the increasing molecular order in the mesophase as thermal agitation diminishes.

The usefulness of any column is limited by the temperature range over which it effectively separates a mixture into its components. For a given nematic stationary phase, the most effective separation is accomplished at the lowest possible temperature, and the degree of separation here is generally greater the higher the nematic-isotropic transition temperature of the mesophase. At the lowest temperature, the molecular order of the mesophase is greatest, since lowering the temperature decreases the kinetic energy of the molecules, resulting in intermolecular forces being more effective. The degree of separation of geometrical isomers is dependent

on the extent of the order in the mesophase.

Mixed Liquid Crystals

An inherent limitation associated with the use of pure nematic compounds as stationary liquid phases is the fixed mesomorphic temperature range within which a given compound is selective. Greater variety and control of operating temperature ranges can be achieved by using mixtures. This, however, introduces a new problem: some disruption of molecular order is inevitable in a nematic mesophase containing two substances with different molecular structures. The effect of adding various solutes to pure nematic compounds has been studied.[8,13,14] If the added substance is structurally dissimilar to the original compound, a small amount is sufficient to destroy liquid crystallinity by disrupting the parallel arrangement of the molecules. If the solute is structurally similar, nematic mesomorphism may persist to a high concentration of the second component. In the case where the second component is also nematogenic, nematic mesomorphism may be exhibited by all compositions.[8]

The mixtures that will be discussed in this thesis are of the latter type, which appears to be the most promising for use in glpc. The following general description of this type of mixture is presented as an introduction to the later discussions of specific examples.

The phase rule[12] can be applied to binary mixtures of nematic substances. Let us assume that the two components

are completely miscible in both the nematic and isotropic states and that all compositions exhibit a nematic mesophase. If the equilibria are plotted on a temperature-composition diagram, under constant pressure, as in Figure 1, the system solid(A)-nematic liquid and solid(B)-nematic liquid will be represented by curves AC and BC, and the system solid(A)-solid(B)-nematic liquid by a point, C. Points A and B

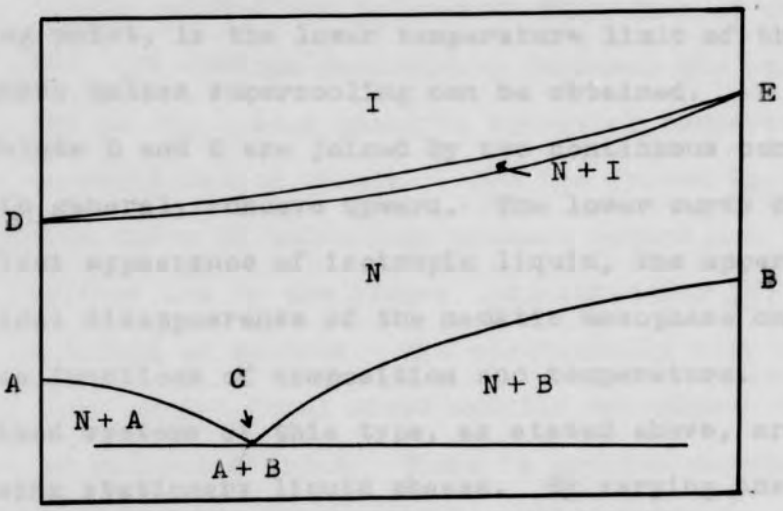


Figure 1. General Phase Diagram of Binary Mixture of Nematic Components

represent the solid-nematic (S-N) transition points, D and E the nematic-isotropic liquid (N-I) transition points of the pure components. Since the crystallization temperature of a liquid is lowered by dissolving another substance in it, it follows that, if a quantity of B is dissolved in nematic A, the temperature at which solid A separates will be below the S-N transition point of pure A. Up to the eutectic

composition, the greater the concentration of B, the lower will be the S-N transition point.

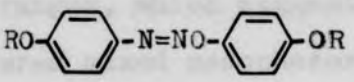
The curve AC represents the compositions of nematic solutions which are in equilibrium, at different temperatures, with solid A. The curve BC serves the same function for nematic solutions in equilibrium with solid B. At the eutectic point C, both solid components exist in equilibrium with a nematic liquid of definite composition. The eutectic melting point, is the lower temperature limit of the nematic mesophase unless supercooling can be obtained.

Points D and E are joined by two continuous curves which are, in general, concave upward. The lower curve designates the first appearance of isotropic liquid, the upper curve the final disappearance of the nematic mesophase on heating, both as functions of composition and temperature.

Mixed systems of this type, as stated above, are promising stationary liquid phases. By varying the composition, the position and length of the nematic temperature range can be controlled. Every composition gives a well-ordered nematic mesophase as indicated by the uniformly high N-I transition temperature. The eutectic mixture is particularly interesting because it can be used at a lower temperature than either pure component, where disruption of the mesophase molecular order by thermal agitation is minimal.

Earlier research in these laboratories showed that

binary mixtures of homologous 4,4'-dialkoxyazoxybenzene (1) are in this category.[8] The phase diagram of the system 1a-1b



1a, R= CH_3
1b, R= C_2H_5
1c, R= n-C_4H_9
1d, R= n-C_6H_{13}

is very much like Figure 1 and the maximum selectivity of the eutectic composition is greater than that of either pure compound. (By maximum selectivity is meant the selectivity displayed at the lowest possible operating temperature, below which crystallization occurs.) For the system 1a-1d, the N-I transition curve is definitely concave upward and the maximum selectivities are in the order: 1d > eutectic > 1a. The results were explained as follows. The structurally very similar 1a and 1b form almost ideal mixed nematic mesophases with a high degree of molecular order. There is greater mesophase disruption when 1a and 1d, which differ significantly in molecular length and polarity, are mixed. This is shown by the concavity in the N-I curve and the mediocre maximum selectivity of the eutectic composition.

The extension of this study to further mixtures of 1 homologs is the subject of this thesis. It was of interest to see if the explanation offered for the 1a-1b and 1a-1d data would hold up for other systems. The homologs 1a, 1b, 1c and 1d were selected for the investigation. The

di-n-propyloxy and di-n-pentyloxy compounds were not included because of their relatively low N-I transition temperatures and short nematic ranges, which suggested that they would produce poorly ordered mixed mesophases:

4,4'-Dialkoxyazoxybenzenes (1)

R	Nematic Range, °C
CH_3 (1a)	118.5-135
C_2H_5 (1b)	138.5-168
n-C_3H_7	116.5-125
n-C_4H_9 (1c)	105-136.5
n-C_5H_{11}	82-124.5
n-C_6H_{13} (1d)	81-129

In summary, the purposes of the study were as follows: (1) To use the selectivity of nematic stationary liquid phases toward solutes on the basis of molecular shape as an index of molecular order in the mesophase. (2) To study the effects of composition and temperature on molecular order in mixtures of homologous dialkoxyazoxybenzenes. (3) To tie the results in with earlier work on this homologous series and to rationalize the data on the basis of the mesophase stabilities and dissimilarities in structure. (4) From a practical standpoint, to assay the significance of the results as they pertain to the achievement of better selectivity with nematic stationary phases.

EXPERIMENTAL

Materials

Three of the 4,4'-dialkoxyazoxybenzenes (1a, 1b, and 1d) are commercially available (Frinton Laboratories). 1a and 1b were purified by recrystallization from benzene before use, 1d was pure as received.

It was necessary to synthesize 1c. The intermediate 4-n-butyloxynitrobenzene was prepared from p-nitrophenol (0.10 mole) and n-butyl bromide (0.16 mole) by a modified Williamson synthesis.[15] The compound was isolated as a crude residue product in quantitative yield and used without further purification in the next step.

4-n-Butyloxynitrobenzene (0.074 mole) was reduced to 1c with $LiAlH_4$ by the method of Dewar and Goldberg[16] in 60% yield. The product was purified by recrystallization from 95% ethanol.

The transition temperatures of the dialkoxyazoxybenzenes used in this work were as follows:

Compound	Solid-Nem., °C	Nematic-Isotropic, °C	Literature Values, °C	Ref.
1a	119.5	135	118.5, 135	17
1b	138.5	169.5	138.5, 168	18
1c	104.5	136	105, 136.5	19
1d	81	129	81, 127	20

The glpc solutes were commercial products which were not purified further. No major contaminants were noted in their chromatograms. The source for methane was natural gas

which was bubbled into n-heptane immediately before injection of the solution into the column. Heavier hydrocarbons were present in the chromatogram, but the methane peak was quite distinguishable.

Procedure and Apparatus

The mixtures used for obtaining the phase diagrams were prepared by weighing the components accurately (nearest mg.) into a microbeaker (0.1 - 0.5 g. samples), melting and stirring to give an intimate blend while allowing to cool. Phase transitions were determined by observation of a small sample in a Nalge-Axelrod melting point apparatus. In this instrument the sample, which is placed between cover glasses (22mm. and 12 mm. dia.) in an aluminum heating block, is illuminated by polarized light and viewed through a 25-power microscope with a rotatable analyzer in the eyepiece so that birefringence can be observed. The temperature was noted from a thermometer inserted into the block, which had been calibrated against compounds of known melting points. A heating rate of about 0.5 ^{o}C per minute was maintained through the transition ranges.

For nonmesomorphic compounds, the melting point is readily determined in this apparatus by noting the temperature at which birefringence disappears. All of the solids in this study melted to birefringent nematic mesophases, making the determination much more difficult. Fortunately, although both the solid and liquid phases were birefringent, their

textures differed. Thus, it was possible to use the complete conversion of grainy solid to smooth, glassy, nematic liquid as the criterion for the melting point. The nematic-isotropic transition point was readily determined from the disappearance of birefringence.

The chromatograms were obtained with an Aerograph Hy-Fi gas chromatograph, Model 600-D, using nitrogen as the carrier gas (flow rate approximately 20 cc./min.) and a flame ionization detector. The injection chamber was at 250 ^{o}C and the sample size was 0.4 microliter of a one percent solution in carbon disulfide for all runs. The very small sample size minimizes disruptive solute effects on the stationary liquid phases. The chromatographic columns were made from annealed copper tubing (3.2 mm. o.d. and 1.8 mm. i.d.) and were 5 m. in length. The tubing was cut, washed with dichloromethane, dried, and weighed on a platform balance (to 0.1 g.). One end was plugged with glass wool and covered with a small plastic cap. The column was then suspended vertically and the packing introduced in small portions through a funnel attached to the top. After each addition, the column was vibrated to encourage downward flow and close packing of the solid particles. The open end was then plugged with glass wool, and the filled column weighed without the plastic cap. The columns were labeled with metal tags. Swagelok fittings were placed on the ends and were made secure when the column was fitted into the chromatograph.

All of the packings contained 15 weight percent of stationary liquid phase on a Chromosorb-W (60-80 mesh) solid support. In the preparation of each column, the Chromosorb-W was weighed into a crystallizing dish and a solution of the liquid phase in dichloromethane was added. By gently shaking the mixture by hand, the liquid was evenly distributed over the Chromosorb. The dichloromethane was then evaporated very slowly to avoid bumping. The mixture was assumed to be dry when the weight was consistent with the complete removal of the solvent. The columns were prepared with the following as the stationary liquid phases: 1c, eutectic mixtures of 1a-1c, 1b-1c, 1c-1d, and 1b-1d, and mixtures rich in the higher melting component for 1b-1c, 1c-1d, and 1b-1d.

To obtain retention times, the column was heated to 15 degrees above the nematic-isotropic transition temperature of the stationary phase and held there for one to two hours. The order in which the samples were run was methane, p-xylene, and m-xylene. The xylenes were run twice at each temperature setting. Retention times were determined at successively lower temperatures, about five degrees apart, until the isotropic-nematic transition had been passed. The interval was then increased to approximately ten degrees. When crystallization occurred, it was obvious from a sharp drop in retention time. An attempt was made to operate at the lowest possible temperature without crystallization.

Usually, retention times were determined at ten to twelve temperatures for each column. The meta and para isomers of ethyltoluene, methylanisole, and dichlorobenzene were also run at the lowest feasible temperature. Methyl, ethyl, and isopropyl benzoate were run at a higher temperature because of their very long retention times.

Retention time was measured by starting the recorder at the moment of sample injection and noting the time for the maximum in the peak. The recorder chart paper was marked in half-minute units (three units per inch) but it was possible to estimate retention time to 0.01 minute by interpolating between lines using a clear plastic ruler with 1/32 inch divisions.

For the calculation of relative retentions, it was necessary to know the retention time of an unabsorbed gas such as air in order to correct for column dead space.[21] The flame ionization detector, while extremely sensitive to organic compounds, has the disadvantage of not giving an air peak so methane was used instead. This is not a satisfactory technique if the stationary liquid phase is nonpolar because then there is some absorption and the retention time of methane is significantly greater than that of air. However, earlier work in these laboratories[8] showed that it is entirely valid for the polar 4,4'-dialkoxyazoxybenzenes. Relative retention (α) was calculated from the equation

$$\alpha = \frac{t_R(\text{sample}) - t_o}{t_R(\text{standard}) - t_o} = \frac{t_R'(\text{sample})}{t_R'(\text{standard})}$$

where t_R is the retention time of the compound whose relative retention is being determined, t_o is the retention time of methane, all determined under the same conditions. The meta isomer was used as the standard for the disubstituted benzenes, the methyl ester for the alkyl benzoates.

RESULTS AND DISCUSSION

Single Compounds

Glpc columns having 1a, 1b, and 1d as the stationary liquid phases were investigated earlier.[8] The results from these studies are contained in the Appendix. In order to complete the data on the pure 1 homologs, a 1c column was prepared. The retention of p-xylene relative to m-xylene (α) was measured at various temperatures. The results for 1a, 1b, 1c and 1d are compared in Figure 2; the retention data for 1c at various temperatures are listed in Table I.

Referring to Figure 2, on cooling the isotropic liquid of 1c, there is a steady increase in α-values. Note that α is greater than unity above the nematic-isotropic temperature, as was observed for 1b and 1d.[8] This supports the proposal of Tolstoi[11] that there is some development of short-range molecular order in the isotropic phase above the nematic-isotropic transition temperature which is the germ of the long-range order characteristic of the anisotropic phase. The fact that 1a does not exhibit an α-value greater than 1.00 above the transition temperature indicates that the parallel arrangement for the molecules of 1a is reduced in the isotropic liquid to an extent that selectivity toward p-xylene relative to m-xylene based on molecular shape is no longer possible.

On further cooling of the nematic mesophase, there is a large increase in α at the transition temperature as the

Table I. Retention Time (t_R) and Relative Retention (α) for m- and p-Xylene on Stationary Liquid Phase of 1c

Temp., °C	t_R, min.			t_R', min.[a]		α for p-Xylene[b]
	p-Xylene	m-Xylene	CH_4	p-Xylene	m-Xylene	
150	6.05 5.98	5.98 5.98	1.14	4.88[c]	4.84	1.008
147	6.28	6.19	1.14	5.14	5.05	1.018
142	6.65 6.61	6.70 6.65	1.14	5.49	5.54	0.991
137	6.52 6.52	6.38 6.33	1.14	5.38	5.22	1.031
135	6.42 6.42	6.33 6.33	1.14	5.28	5.19	1.017
133	6.52 6.47	6.38 6.38	1.14	5.40	5.29	1.021
131	6.66 6.70	6.50 6.50	1.09	5.59	5.31	1.053
124	7.09 7.09	6.84 6.80	1.09	6.00	5.63	1.066
117	7.84 7.84	7.23 7.50	1.09	6.75	6.28	1.075

Table I.(Continued)

Temp., °C	t_R, min.			t_R', min.[a]		α for p-Xylene[b]
	p-Xylene	m-Xylene	CH_4	p-Xylene	m-Xylene	
116	7.94	7.61	1.05	6.89	6.56	1.050
112	8.56 8.52	8.14 8.09	1.09	7.45	7.03	1.060
111	8.58 8.56	8.09 8.09	1.09	7.48	7.00	1.069
108	9.09 9.14	8.61 8.61 8.56	1.09	8.14	7.50	1.085
106[d]	8.19 8.05	7.89 7.52 7.42	1.09			
104[d]	7.19 6.98	6.42	1.09			

a. t_R (Xylene) - t_R (CH_4).

b. m-Xylene = 1.000.

c. Average for two runs.

d. Crystallization has begun.

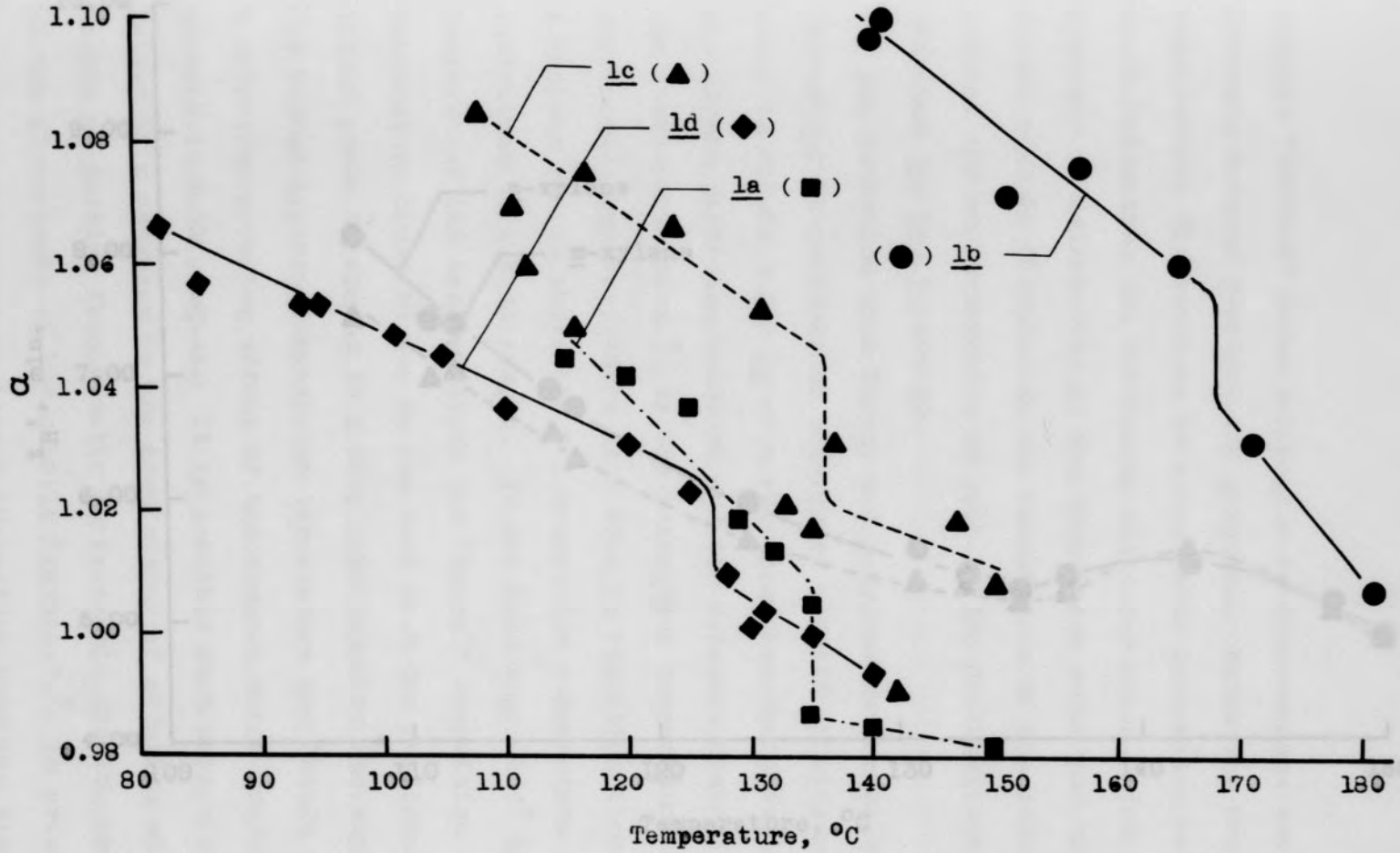


Figure 2. Relative Retention (α) of p-Xylene (m-Xylene = 1.00) at Various Temperatures on Stationary Liquid Phases of 1a, 1b, 1c and 1d

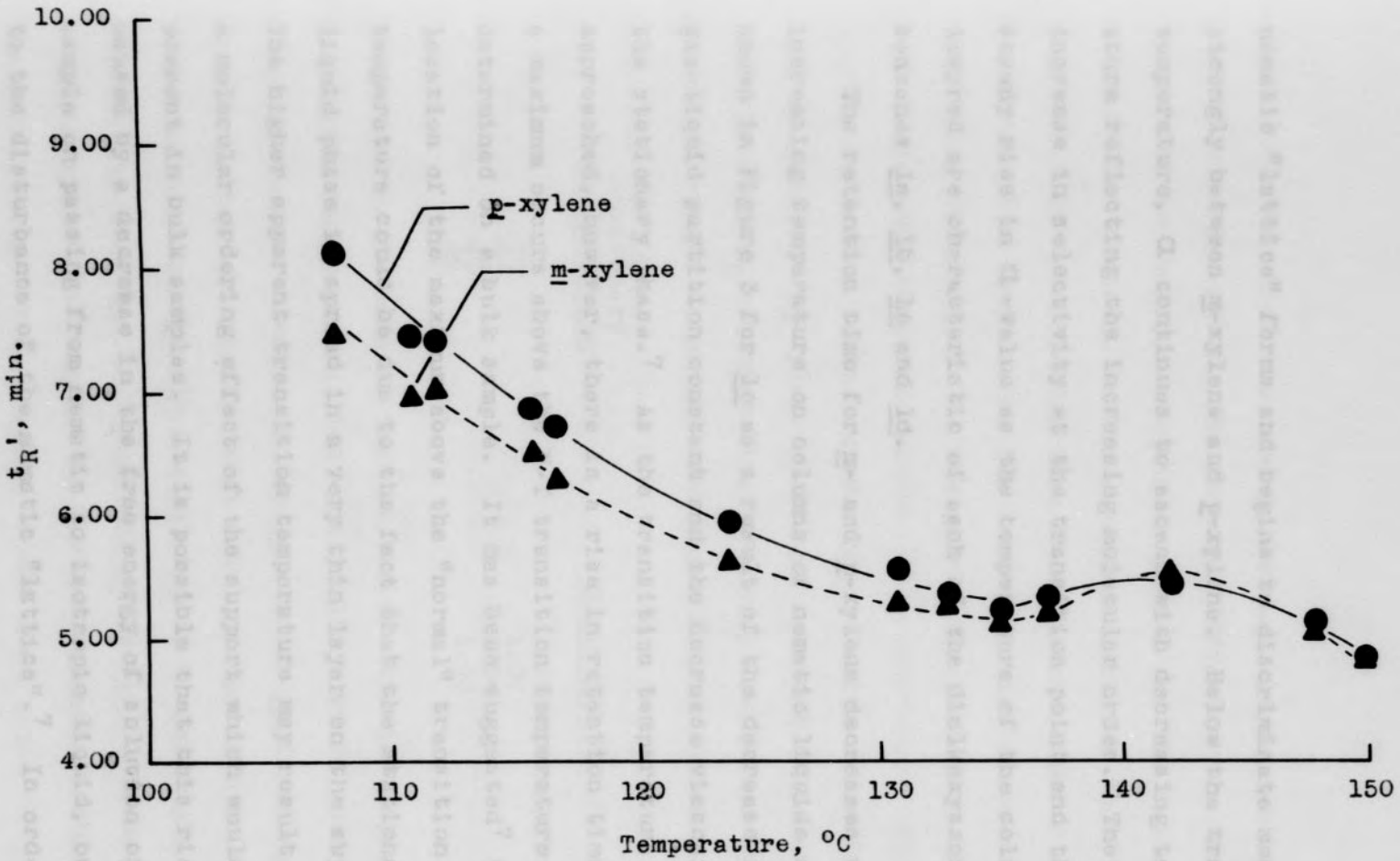


Figure 3. Retention Time (t_R') of m- and p-Xylene on Stationary Liquid Phase of 1c at Various Temperatures

nematic "lattice" forms and begins to discriminate more strongly between m-xylene and p-xylene. Below the transition temperature, α continues to ascend with decreasing temperature reflecting the increasing molecular order. The sharp increase in selectivity at the transition point and the steady rise in α-value as the temperature of the column is lowered are characteristic of each of the dialkoxyazoxybenzenes 1a, 1b, 1c and 1d.

The retention time for m- and p-xylene decreases with increasing temperature on columns of nematic liquids as is shown in Figure 3 for 1c as a result of the decrease in the gas-liquid partition constant and the decrease viscosity of the stationary phase.[7] As the transition temperature is approached, however, there is a rise in retention time, and a maximum occurs above the N-I transition temperature as determined on a bulk sample. It has been suggested[7] that the location of the maximum above the "normal" transition temperature could be due to the fact that the stationary liquid phase is spread in a very thin layer on the support. The higher apparent transition temperature may result from a molecular ordering effect of the support which would not be present in bulk samples. It is possible that this rise is caused by a decrease in the free energy of solution of the sample on passing from nematic to isotropic liquid, owing to the disturbance of the nematic "lattice".[7] In order for the solute molecules to insert themselves into the liquid

crystal "lattice" of the nematic solvent there must be a loss of entropy, making the process difficult. As the transition to isotropic liquid is passed and the solvent becomes less ordered, an increase in solubility should result. With a continuing rise in temperature above the N-I transition temperature the retention time decreases again reflecting the decrease in the gas-liquid partition constant with increasing temperature.

The following table compares the relative retention (α) of p-xylene (m-xylene = 1.00) at constant temperature (and, therefore, constant kinetic energy) exhibited by the different single component stationary liquid phases.

Stationary Liquid Phase	α at 120 °C
1b	1.12 (extrapolated)
1c	1.07
1a	1.04
1d	1.03

The order is the same as that of the nematic-isotropic transition temperatures (168 > 136.5 > 135 > 129 °C) but the large difference between α for 1c and for 1a is unexpected on this basis. It appears that alkyl groups with an even number of carbons (1b, 1c and 1d) impart surprisingly good selectivity relative to the methyl group (1a) in consideration of the alkyl chain length. In further support of this is the small change in α between 1a and 1d.

The lower operating temperature of a nematic stationary

liquid phase is reached when crystallization begins. This is noted experimentally by a sharp drop in retention time for m- or p-xylene (see Appendix, Table V). As crystallization proceeds, the amount of liquid phase is reduced and the vapors passing through the column necessarily are retained less strongly. The lower limit for 1c is reached at 108 °C. This is higher than the melting point determined on a bulk sample (104.5 °C). A satisfactory explanation for this discrepancy is not apparent.

The maximum α-value (p-xylene/m-xylene) possible for a given nematic stationary phase is attained at the lowest possible temperature. For the four dialkoxyazoxybenzenes studied, the maximum α-values are listed below with the corresponding temperatures at which they were determined:

Stationary Liquid Phase	Maximum α-Value	Temp., °C
1b	1.100	141
1c	1.085	108
1a	1.045	115
1d	1.066	88

For the 1 homologs in which R has an even number of carbon atoms, the maximum α-values follow the order of N-I transition temperatures: 1b > 1c > 1d. The α_{max} of 1a, however, falls out of line severly, being much lower than 1d. This phenomenon is easily explained by noting Figure 2. At a given temperature below the N-I transition point of 1a, the selectivity of 1a is invariably greater than that of 1d as

would be expected from the respective transition temperatures. At 115 °, 1a crystallizes, while 1d remains liquid to 82 °. This lower limit allows 1d to surpass 1a in maximum selectivity.

Binary Mixtures

Table II describes the glpc columns, with 1c and binary mixtures of 1 homologs as stationary liquid phases, which were prepared and studied. The phase diagrams, Figures 4, 6, 8 and 10, show that, for all compositions, these binary systems are nematogenic.

1b-1d

Of the compounds studied, 1b has the most stable crystalline lattice and nematic mesophase, while 1d has the least. This undoubtedly reflects a significant difference in molecular polarity and, therefore, it is not surprising that the phase diagram for the 1b-1d system (Figure 4) indicates some incompatibility of the components. Thus, addition of 1d to 1b causes only a slight lowering of the melting point until the eutectic composition is approached; the N-I transition temperature range is large in this composition region; the equimolar mixture has the shortest nematic range of any composition; and addition of 1b to 1d causes little change in the melting and N-I transition points.

The results indicate that the eutectic mixture should exhibit a molecular order comparable to 1d. The second composition which was studied (63.6 mole percent 1b)

Table II. Description of Gas-Liquid Partition Chromatography Columns

Column Number	Stationary Liquid Phase[a]	Melting Range, °C	Nematic-Isotropic Transition Range, °C	Weight of Packing, g.
AA-4	lc (100)	104.5	136	4.6
S-4	lb-ld (22.2-77.8) (eutectic)	76-79	131-131.5	4.3
S-3	lb-ld (63.6-36.4)	76-129	141.5-150.0	5.3
S-6	la-lc (36.0-64.0) (eutectic)	84-85	130.0-130.5	4.9
S-5	lb-lc (34.1-65.9) (eutectic)	85.5-88	143.5-145	4.8
S-1	lb-lc (55.3-44.7)	86-118.5	148-153.5	4.7
S-7	lc-ld (47.9-52.1) (eutectic)	67.5-68	129.5-130.5	4.6
S-2	lc-ld (54.8-45.2)	67.5-76	130-131.5	4.9

a. Indicated compositions are in mole percent.

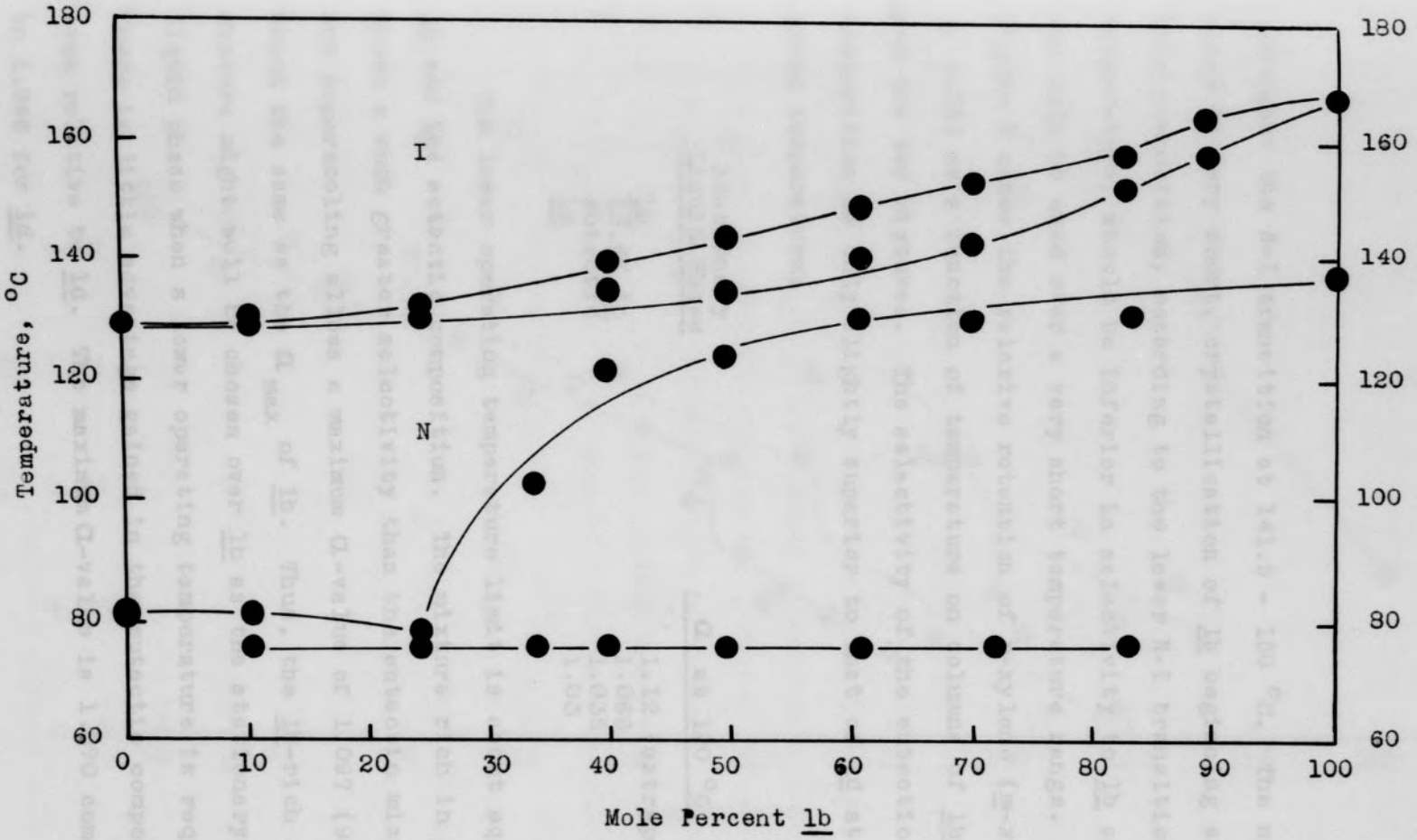


Figure 4. Phase Diagram of System 1b-1d (N= nematic, I= isotropic)

undergoes the N-I transition at 141.5 - 150 °C. The nematic range is very short, crystallization of 1b beginning at 130 °C. This composition, according to the lower N-I transition temperature, should be inferior in selectivity to 1b and can only be used over a very short temperature range. Figure 5 shows the relative retention of p-xylene (m-xylene = 1.00) as a function of temperature on columns of 1b, 1d, and the two mixtures. The selectivity of the eutectic composition is only slightly superior to that of 1d at a given temperature:

Stationary Liquid Phase	α at 120 °C
1b	1.12 (extrapolated)
63.6% 1b eutectic	1.066
1d	1.035
	1.03

The lower operating temperature limit is about equal for 1d and the eutectic composition. The mixture rich in 1b shows a much greater selectivity than the eutectic mixture, and supercooling allows a maximum α-value of 1.097 (98 °C), about the same as the α_{max} of 1b. Thus, the 1b-rich mixture might well be chosen over 1b as the stationary liquid phase when a lower operating temperature is required. There is little advantage gained in the eutectic composition even relative to 1d. The maximum α-value is 1.070 compared to 1.066 for 1d.

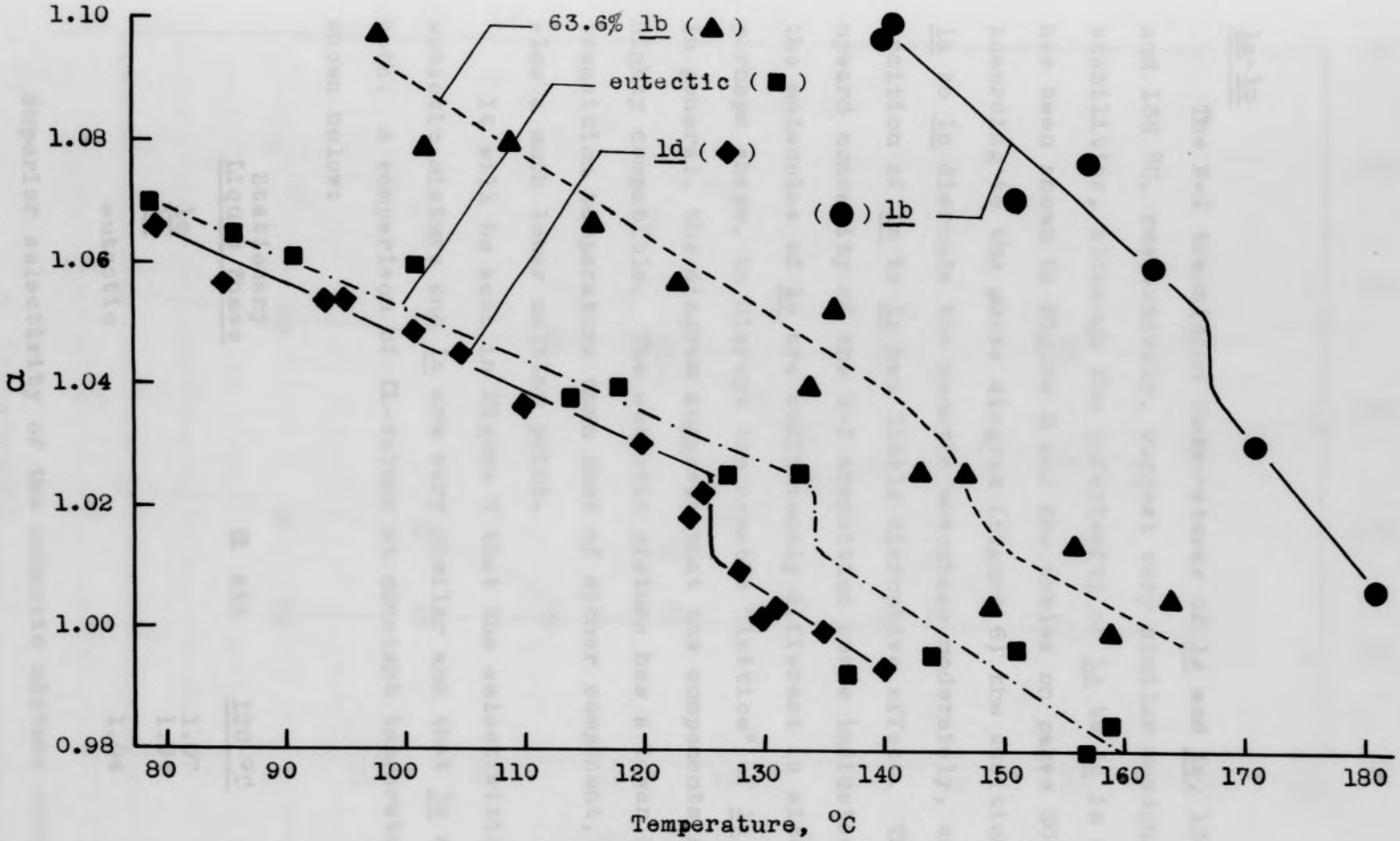


Figure 5. Relative Retention (α) of p-Xylene (m-Xylene = 1.00) at Various Temperatures on Stationary Liquid Phases of 1b, 1d, and Mixtures of 1b-1d

1a-1c

The N-I transition temperatures of 1a and 1c, 135 °C and 136 °C, respectively, suggest very similar mesophase stabilities, although the inferiority of 1a to 1c in selectivity has been shown in Figure 2 and the tables on pages 30 and 31. According to the phase diagram (Figure 6) the addition of 1a to 1c disrupts the nematic mesophase moderately, and the addition of 1c to 1a has little disruptive effect. The upward concavity of the N-I transition curve indicates that the molecules of 1a are sufficiently different in size, and perhaps shape, to disrupt the nematic "lattice" of 1c slightly. In general, the diagram suggests that the components are highly compatible. The eutectic mixture has a lower N-I transition temperature than that of either component, but also a much lower melting point.

It will be seen in Figure 7 that the selectivities of the eutectic mixture and 1a are very similar and that 1c surpasses both. A comparison of α-values at constant temperature is shown below:

Stationary Liquid Phase	α at:	120 °C	110 °C
1c		1.07	1.08
1a		1.04	1.06 (extrapolated)
eutectic		1.04	1.05

Superior selectivity of the eutectic mixture over 1a is realized only below the crystallization temperature of 1a.

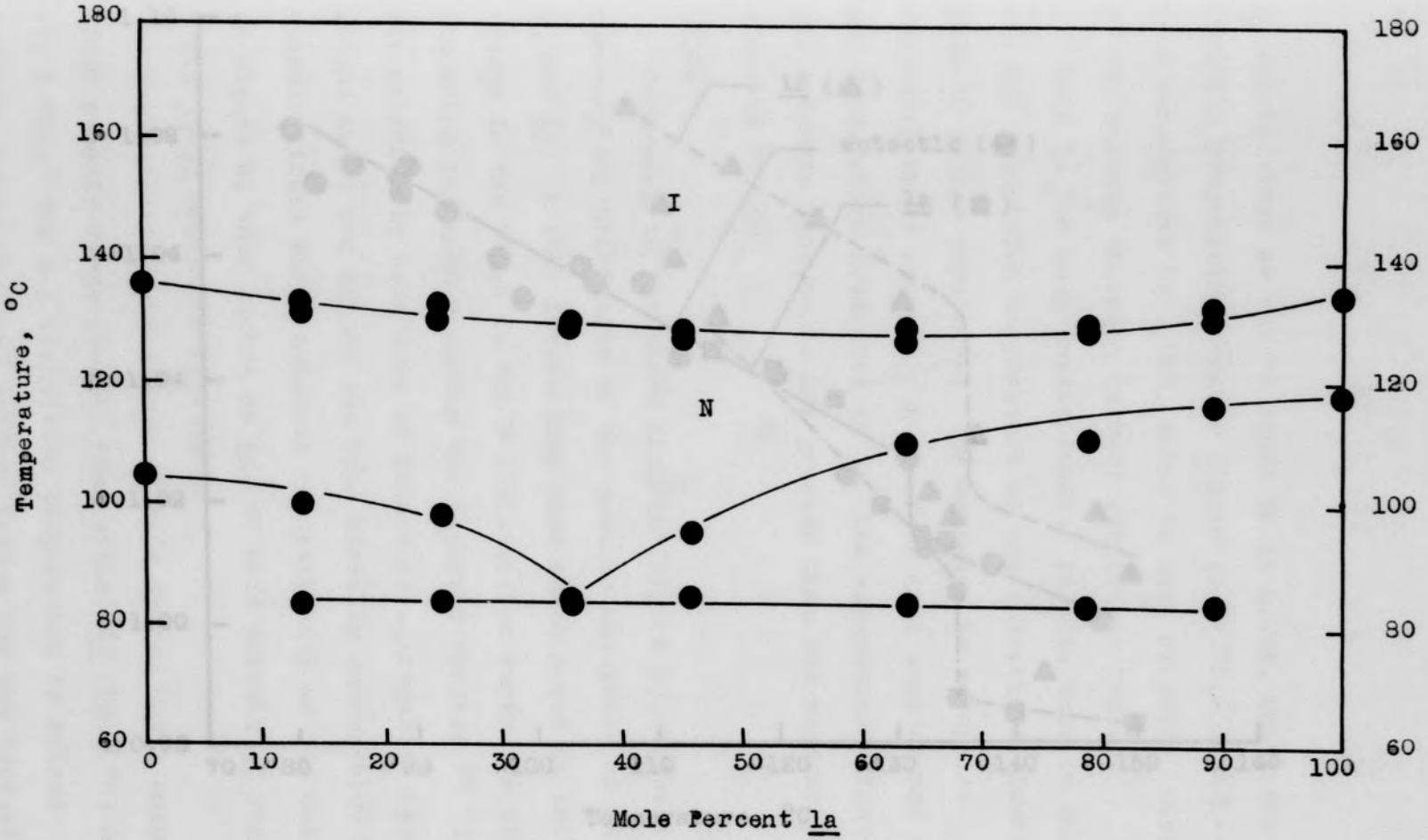


Figure 6. Phase Diagram of System la-lc (N= nematic, I= isotropic)

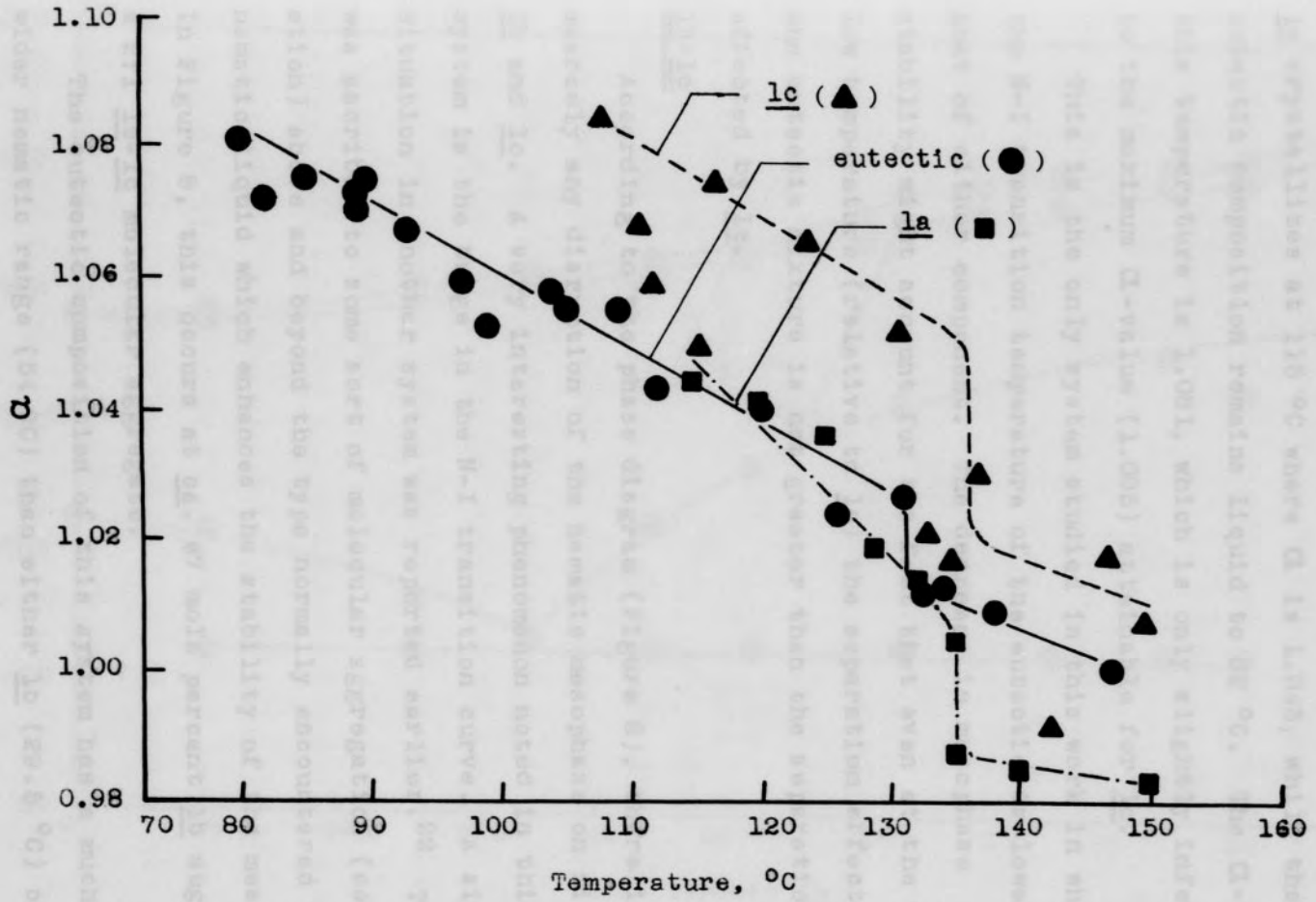


Figure 7. Relative Retention (α) of p-Xylene (m-Xylene = 1.00) on Stationary Liquid Phases of la, lc, and Eutectic Mixture of la-lc at Various Temperatures

1a crystallizes at 115 °C where α is 1.045, while the eutectic composition remains liquid to 82 °C. The α-value at this temperature is 1.081, which is only slightly inferior to the maximum α-value (1.085) attainable for 1c.

This is the only system studied in this work in which the N-I transition temperature of the eutectic is lower than that of either component. The decrease in mesophase stability might account for the fact that even at the very low temperature (relative to 1c) the separation effected by the eutectic mixture is not greater than the separation effected by 1c.

1b-1c

According to the phase diagram (Figure 8), there is scarcely any disruption of the nematic mesophase on mixing 1b and 1c. A very interesting phenomenon noted in this system is the bulge in the N-I transition curve. A similar situation in another system was reported earlier.[22] This was ascribed to some sort of molecular aggregation (complexation) above and beyond the type normally encountered in a nematic liquid which enhances the stability of the mesophase. In Figure 8, this occurs at ca. 67 mole percent 1b suggesting a 2:1 1b-1c molecular aggregate.

The eutectic composition of this system has a much wider nematic range (54 °C) than either 1b (29.5 °C) or 1c (31.5 °C). The N-I transition temperature is raised relative to 1c, but the primary factor for the increased

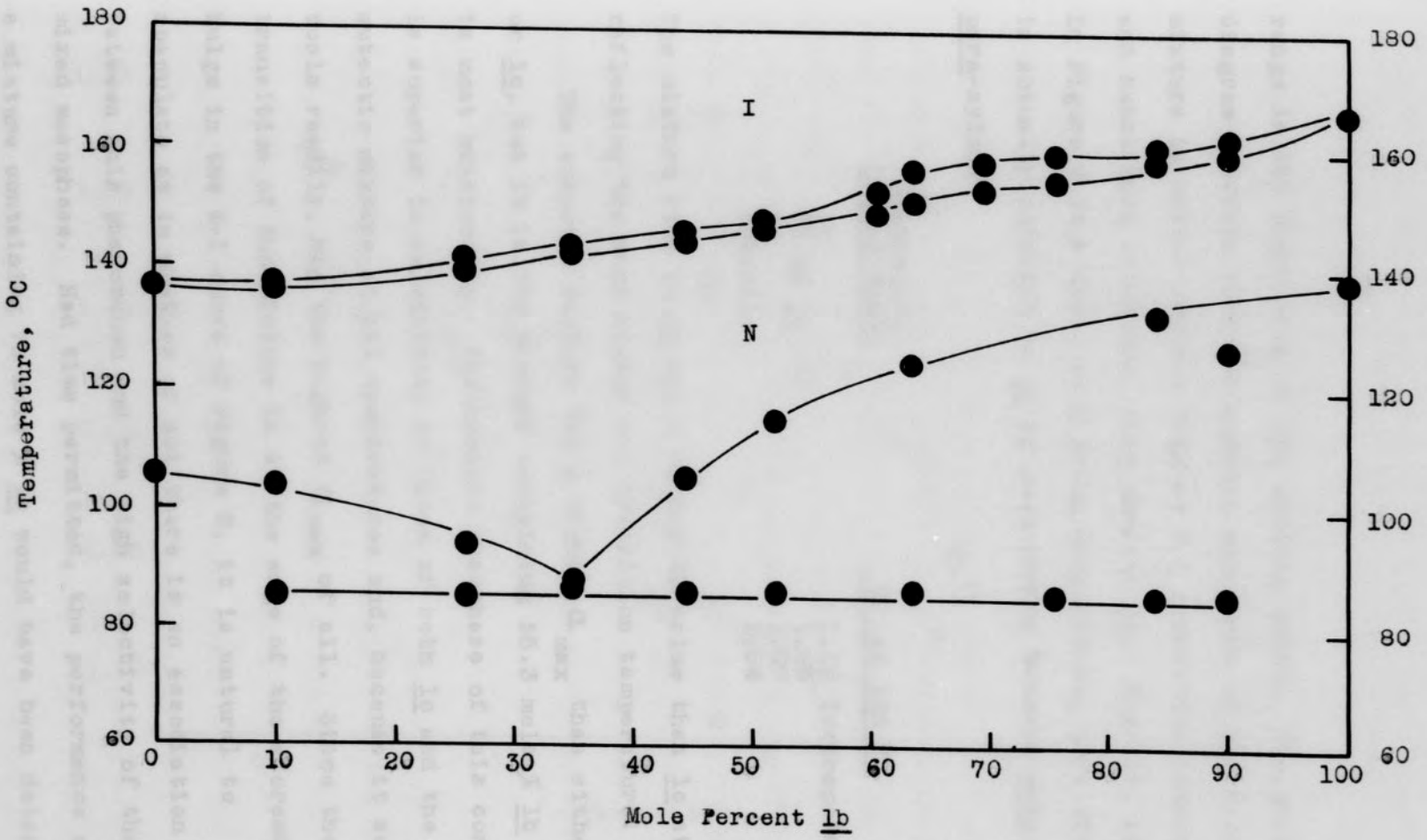


Figure 8. Phase Diagram of System 1b-1c (N = nematic, I = isotropic)

range is the depression of the melting point. The phase diagram predicts that the nematic mesophase of the eutectic mixture is better ordered (higher N-I transition temperature), and hence more selective, than nematic 1c. However, the data in Figure 9 show that, at a given temperature, this mixture is actually inferior to 1c in selectivity between meta- and para-xylene:

Stationary Liquid Phase	α at 120 °C
1b	1.12 (extrapolated)
55.3% 1b	1.08
1c	1.07
eutectic	1.06

The mixture rich in 1b has a higher α-value than 1c at 120 °C, reflecting the much higher N-I transition temperature.

The eutectic mixture has a higher α_{max} than either 1b or 1c, but it is the mixture containing 55.3 mole % 1b that is most outstanding. The nematic mesophase of this composition is superior in selectivity to those of both 1c and the eutectic mixture at all temperatures and, because it supercools readily, has the highest α_{max} of all. Since the N-I transition of the mixture is at the edge of the aforementioned bulge in the N-I curve of Figure 8, it is natural to speculate as to whether or not there is an association between this phenomenon and the high selectivity of the mixed mesophase. Had time permitted, the performance of a mixture containing 70 mole % 1b would have been determined

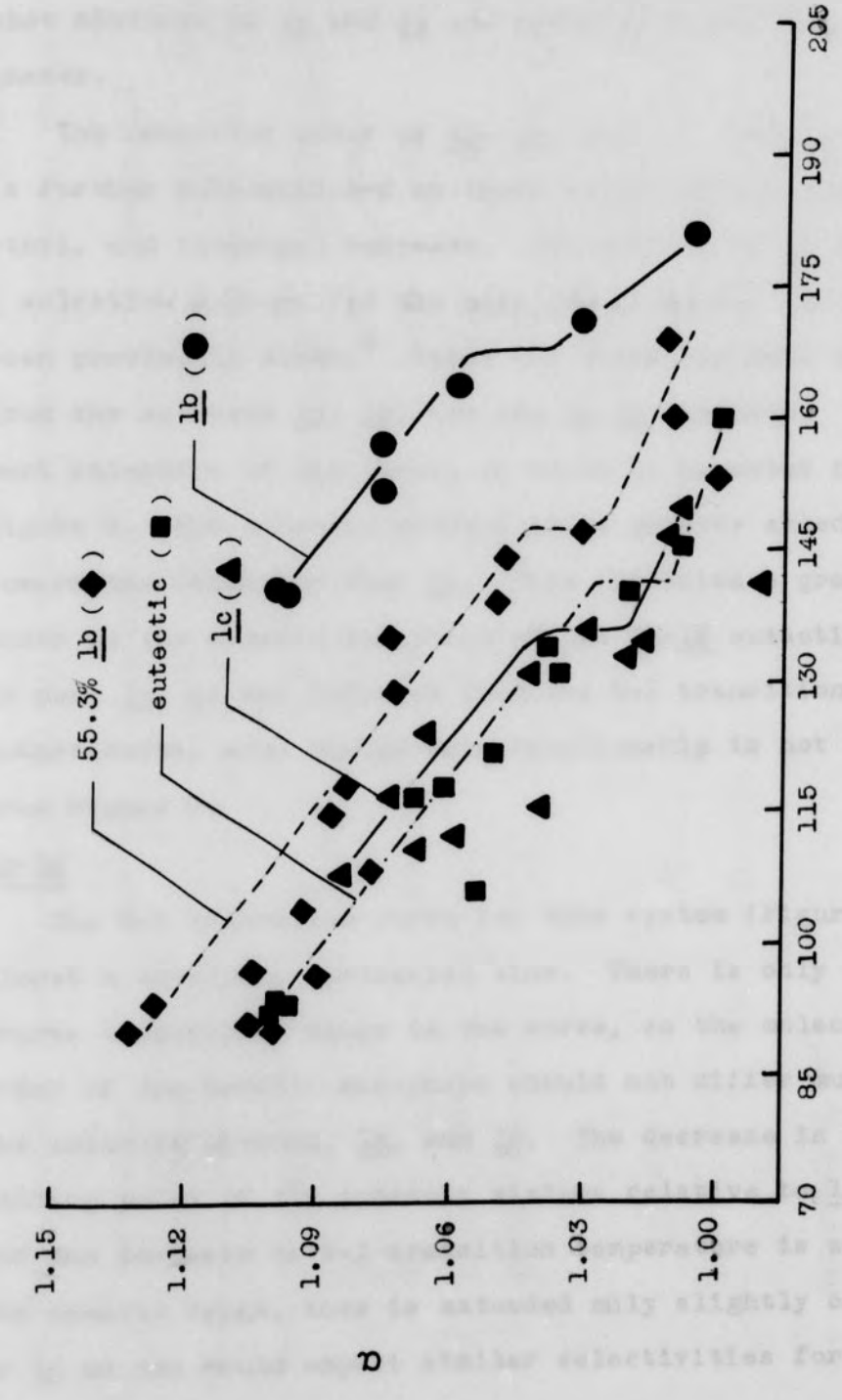


Figure 9. Relative Retention (α) of p-Xylene (m-Xylene=1.00) on Stationary Liquid Phases of 1b, 1c, and Mixtures of 1b-1c at Various Temperatures

to check this point. In any event, the present data show that mixtures of 1b and 1c are promising stationary liquid phases.

The molecular order of 1b, 1c, and the eutectic mixture is further substantiated by their selectivities toward methyl, ethyl, and isopropyl benzoate. The ability of 1b to act as a selective solvent for the more linear methyl ester has been previously shown.[8] Table III lists the data obtained from the solvents 1b, 1c, and the 1b-1c eutectic. 1b is the most selective of the three, as would be expected from Figure 9. The eutectic mixture shows greater selectivity toward the benzoates than 1c. This indicates a greater order in the nematic mesophase of the 1b-1c eutectic than in pure 1c, as was inferred from the N-I transition temperatures, even though this relationship is not apparent from Figure 9.

1c-1d

The N-I transition curve for this system (Figure 10) is almost a straight, horizontal line. There is only a six degree temperature range in the curve, so the molecular order of the nematic mesophase should not differ much for the eutectic mixture, 1c, and 1d. The decrease in the melting point of the eutectic mixture relative to 1d is small, and the increase in N-I transition temperature is even less. The nematic range, then is extended only slightly compared to 1d so one would expect similar selectivities for the two

Table III. Relative Retentions (α) of m- and p-Xylene and of Methyl, Ethyl, and Isopropyl Benzoate in Silicone, 1b, 1c, 1b-1c and 1b-1d Stationary Liquid Phases

Stationary Liquid Phase	Temp., °C	Xylenes		Benzoates		
		meta	para	Methyl	Ethyl	Isopropyl
SE - 30 Silicone[a]	104	1.00	0.99	1.00	1.64	1.98
1b	141	1.00	1.10	1.00	1.23	1.08
1c	125	1.00	1.062[b]	1.00	1.38	1.37
1b-1c (eutectic)	131	1.00	1.041[c]	1.00	1.31	1.27
1b-1d (eutectic)	114	1.00	1.038	1.00	1.44	1.44

a. Reference 8.

b. Value from Figure 2.

c. Value from Figure 5.

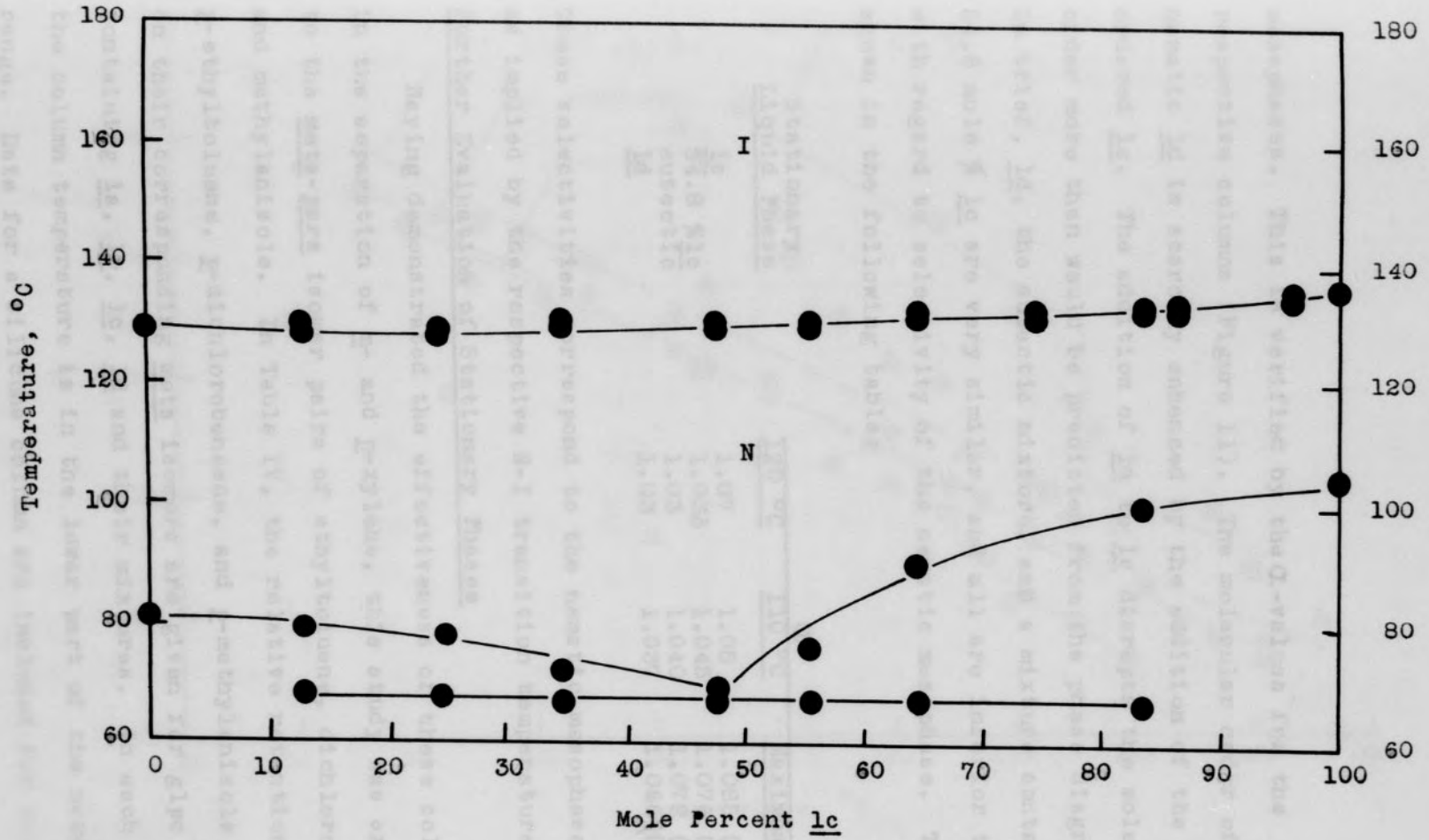


Figure 10. Phase Diagram of System lc-ld (N= nematic, I= isotropic)

mesophases. This is verified by the α-values for the respective columns (Figure 11). The molecular order of nematic 1d is scarcely enhanced by the addition of the more ordered 1c. The addition of 1d to 1c disrupts the molecular order more than would be predicted from the phase diagrams. In brief, 1d, the eutectic mixture, and a mixture containing 54.8 mole % 1c are very similar, and all are inferior to 1c with regard to selectivity of the nematic mesophase. This is shown in the following table:

Stationary Liquid Phase	α 120 °C	α 110 °C	α Maximum
1c	1.07	1.08	1.085 (108 °C)
54.8 %1c eutectic	1.035	1.045	1.076 (72 °C)
	1.03	1.040	1.072 (76 °C)
1d	1.03	1.037	1.066 (80 °C)

These selectivities correspond to the nematic mesophase order as implied by the respective N-I transition temperatures.

Further Evaluation of Stationary Phases

Having demonstrated the effectiveness of these columns in the separation of m- and p-xylene, this study was extended to the meta-para isomer pairs of ethyltoluene, dichlorobenzene, and methylanisole. In Table IV, the relative retentions of p-ethyltoluene, p-dichlorobenzene, and p-methylanisole based on their corresponding meta isomers are given for glpc columns containing 1a, 1b, 1c, 1d and their mixtures. In each case, the column temperature is in the lower part of the nematic range. Data for a silicone column are included for comparison.

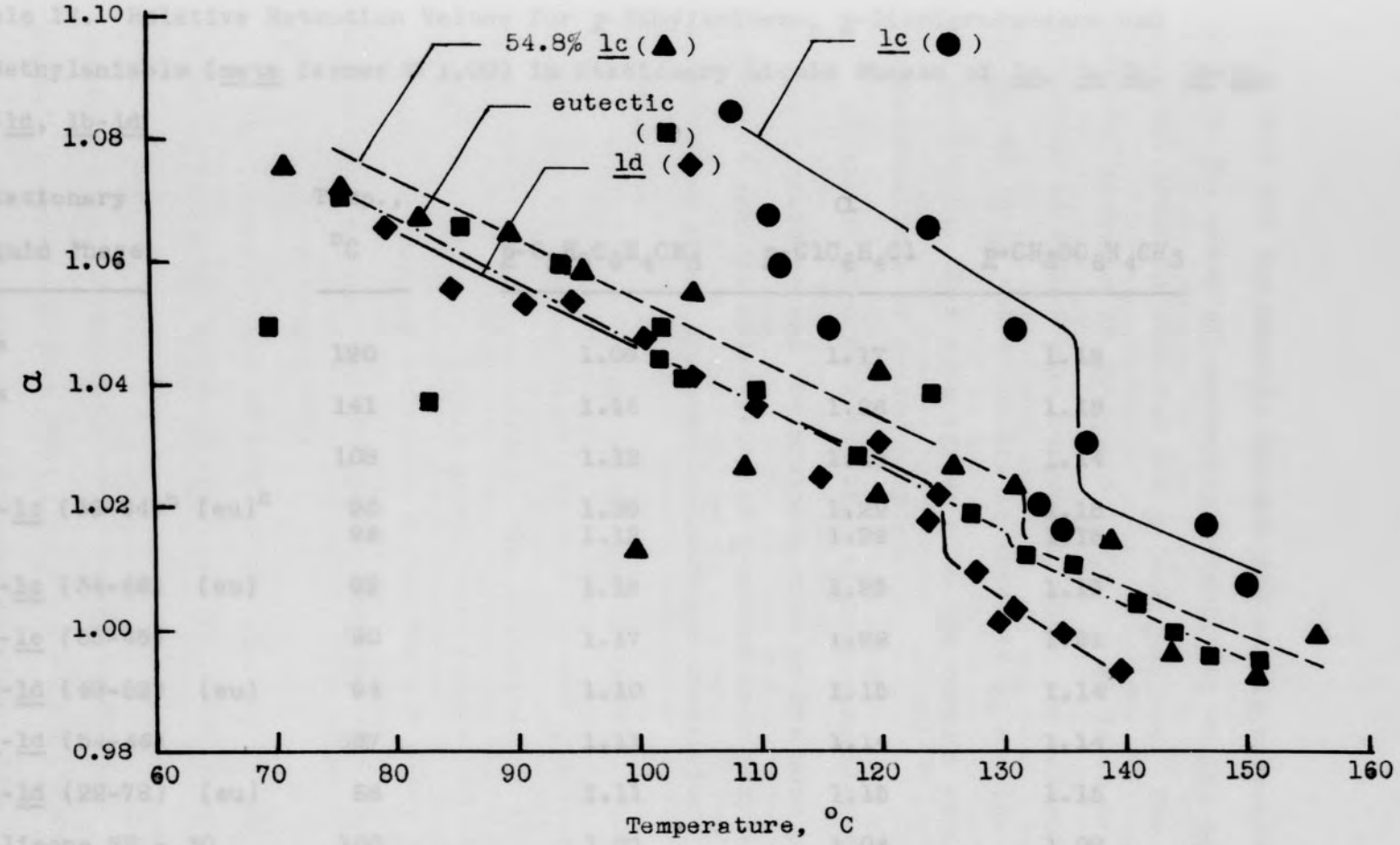


Figure 11. Relative Retention (α) of p-Xylene (m-Xylene = 1.00) on Stationary Liquid Phases of lc, ld, and Mixtures of lc-ld at Various Temperatures

Table IV. Relative Retention Values for p-Ethyltoluene, p-Dichlorobenzene and p-Methylanisole (meta Isomer = 1.00) in Stationary Liquid Phases of 1c, 1a-1c, 1b-1c, 1c-1d, 1b-1d

Stationary Liquid Phase	Temp., °C	α p-$C_2H_5C_6H_4CH_3$	α p-ClC_6H_4Cl	α p-$CH_3OC_6H_4CH_3$
1a[a]	120	1.09	1.17	1.12
1b[a]	141	1.15	1.26	1.18
1c	108	1.12	1.18	1.14
1a-1c (36-64)[b] (eu)[c]	90	1.29	1.22	1.18
	96	1.12	1.22	1.15
1b-1c (34-66) (eu)	92	1.19	1.25	1.19
1b-1c (55-45)	90	1.17	1.22	1.21
1c-1d (48-52) (eu)	94	1.10	1.15	1.14
1c-1d (54-46)	87	1.11	1.14	1.14
1c-1d (22-78) (eu)	86	1.11	1.15	1.15
Silicone SE - 30	100	1.01	1.04	1.02

a. Reference 8.

b. Mole percent.

c. eu = eutectic.

Note that all the nematic liquids are highly selective, and fall in the order of decreasing selectivity -- 1b, 1c, 1a -- the same order as observed for m- and p-xylene. The eutectic mixtures of 1a-1c and 1b-1c are at least as selective as either pure component, while the selectivity of 1c-1d and 1b-1d eutectics are inferior to 1c and 1d, respectively. This also agrees with the results obtained from separations of m- and p-xylene.

It should also be noted that without exception the eutectic mixtures and the mixtures rich in the more ordered component exhibit selectivity of p-xylene over m-xylene at temperatures above the nematic-isotropic transition temperature.

SUMMARY AND CONCLUSIONS

The phase diagrams of the systems 1b-1d, 1a-1c, 1b-1c, and 1c-1d were constructed by determining the melting ranges and nematic-isotropic transition ranges of various compositions of the binary systems. It was found, as is shown in Figures 4, 6, 8, and 10, that for all compositions these systems give nematic mesophases. In general, the order of the nematic mesophase of the mixtures was intermediate between that of the two pure components.

Binary mixtures from these systems and also pure 1c were used as stationary liquid phases in glpc and, in this manner, the selectivities of their nematic mesophases toward solutes on the basis of molecular shape were determined. The separation of the positional isomers, m- and p-xylene, served as a test for the selectivity. The selectivities of the different stationary liquid phases were determined at temperatures ranging from five to ten degrees above the N-I transition temperature through the nematic range to the crystallization temperature.

The selectivities of nematic 1a, 1b, 1c, and 1d were found to be in the order 1b > 1c > 1a > 1d. This order is the same as that of their N-I transition temperatures, which is an index of molecular regularity in the mesophase. Thus, the results support the idea that selectivity is a function of molecular order. The data indicate, however, that the N-I transition temperature is only a rough indicator of order.

E. g., 1c and 1a have almost identical N-I transition points (136.5° and 135°, respectively), but 1c is far more selective. The results suggest that 4,4'-dialkoxyazoxybenzenes in which the alkyl group has an odd number of carbon atoms have more poorly ordered nematic mesophases than would be predicted from their N-I transition points. This should be checked using the dipropyloxy, dipentyloxy and diheptyloxy homologs.

The following table summarizes the glpc results in terms of α_{max}, the value of the relative retention of p-xylene (m-xylene = 1.00) obtained for a nematic stationary liquid phase at its lowest possible operating temperature. This is an excellent criterion of maximum selectivity and molecular order. Earlier results for the 1a-1b and 1a-1d systems[8] are included for comparison. It should be stressed that the separation of m- and p-xylene by glpc is a classically difficult one and that α-values greater than 1.05 are noteworthy. On this basis, most of the phases in the table can be classified as highly selective and several are exceptionally so.

Stationary Liquid Phase	α_{max}
1b-1c (55 mole % 1b)	1.13
1b-1a (49 mole % 1b) (eutectic)[a]	1.12
1b-1c (35 mole % 1b) (eutectic)	1.11
1b	1.10
1b-1d (64 mole % 1b)	1.10
1c	1.085
1c-1a (64 mole % 1c) (eutectic)	1.08
1c-1d (55 mole % 1c)	1.08

Stationary Liquid Phase (cont.)	α_{max} (cont.)
1b-1d (24 mole % 1b) (eutectic)	1.07
1c-1d (48 mole % 1c) (eutectic)	1.07
1d	1.07
1d-1a (73 mole % 1d) (eutectic)	1.07
1d-1a (66 mole % 1d) (eutectic)	1.06
1d-1a (39 mole % 1d) (eutectic)	1.05
1a	1.045
1d-1a (18 mole % 1d)	1.03

a. 1b-rich mixture was not studied.

The table shows that the α_{max} values of the pure homologs are in the order 1b > 1c > 1d > 1a. On examining the table further, one is struck by the fact that the order in which the pure components contribute to the selectivity of mixed mesophases is also 1b > 1c > 1d > 1a. That is, 1b mixtures are, in general, more selective than 1c mixtures, etc. Another interesting feature of the data is that, in the systems 1b-1c, 1b-1d, 1c-1d and 1d-1a, selectivity increases with increasing concentration of the more selective component. Similarly, the 1c-1a eutectic mixture, which has a high content of 1c, is very selective ($\alpha_{max} = 1.08$). These results negate the rule of thumb that the eutectic composition is likely to be the most selective mixture in a binary nematic system.[8] Apparently, a balance must be struck between the molecular ordering effects of the more selective component and of the minimum operating temperature in order to achieve maximum selectivity. It seems likely that 1b-1a mixtures rich in 1b, which have not been studied, would also be highly effective stationary phases.

The data in the table further show that nematic mixtures of 1 homologs are most selective when the components are highly selective and have alkyl groups of comparable length. Thus, 1b-1c (R= C_2H_5 and C_4H_9) and 1b-1a (R= C_2H_5 and CH_3) mixtures have the highest α_{max} values. Even when the alkyl groups differ considerable in length, as in 1b-1d mixtures (R= C_2H_5 and C_6H_{13}), the performance is excellent if one component is highly selective and present in high concentration. This is reasonable in that one would expect (1) a selective homolog to have a strong molecular ordering effect in a mixed nematic mesophase, and (2) minimum disruption of a mixed mesophase when the components are structurally similar.

BIBLIOGRAPHY

1. G. Friedel, Ann. Phys. (Paris), 18, 273 (1922); Chem. Abstr., 17, 3267 (1923).

2. G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals," Academic Press, London-New York, 1962.

3. E. Bose, Phys. Z., 10, 32 and 230 (1909); Chem. Abstr., 3, 140 (1909).

4. L. S. Ornstein and W. Kast, Trans. Faraday Soc., 29, 931 (1933).

5. Reference 2, p. 175.

6. H. Kelker, Z. Anal. Chem., 198, 254 (1963); Chem. Abstr., 60, 3550 (1964).

7. M. J. S. Dewar and J. P. Schroeder, J. Amer. Chem. Soc., 86, 5235 (1964); J. Org. Chem., 30, 3485 (1965).

8. J. P. Schroeder, D. C. Schroeder, and M. Katsikas, "Nematic Mixtures as Stationary Liquid Phases in Gas-Liquid Chromatography," in J. F. Johnson and R. S. Porter, Eds., "Liquid Crystals and Ordered Fluids," Plenum Publishing Corp., New York, in press.

9. M. J. S. Dewar, J. P. Schroeder, and D. C. Schroeder, J. Org. Chem., 32, 1692 (1967).

10. S. Dal Nogare and R. S. Juvet, Jr., "Gas-Liquid Chromatography," Interscience, New York, 1962, p. 22.

11. N. A. Tolstoi, J. Expt. Theoret. Phys. (U. S. S. R.), 17, 724 (1947); Chem. Abstr., 42, 5322 (1948).

12. A. Findley, A. N. Campbell, and N. O. Smith, "The Phase Rule and Its Applications," Dover Publications, Inc., New York, 1951, pp. 1-19 and 133-188.

13. J. S. Dave and M. J. S. Dewar, J. Chem. Soc., 4305 (1955).

14. J. S. Dave and M. J. S. Dewar, ibid., 4616 (1954).

15. G. W. Gray and B. Jones, ibid., 1467 (1954).

16. M. J. S. Dewar and R. S. Goldberg, Tetrahedron Letters, 24, 2717 (1966).

17. W. Davies and R. A. R. Down, J. Chem. Soc., 589 (1929); R. S. Porter and J. F. Johnson, J. Phys. Chem., 66, 1826 (1962).

18. I. F. Homfray, J. Chem. Soc., 97, 1669 (1910).

19. W. Maier and G. Englert, Z. Phys. Chem. (Frankfurt), 19, 168 (1959).

20. C. Weygand and R. Gabler, J. Prakt. Chem., 155, 332 (1940).

21. Reference 10, p. 24.

22. J. P. Schroeder and D. C. Schroeder, J. Org. Chem., 33, 591 (1968).

APPENDIX

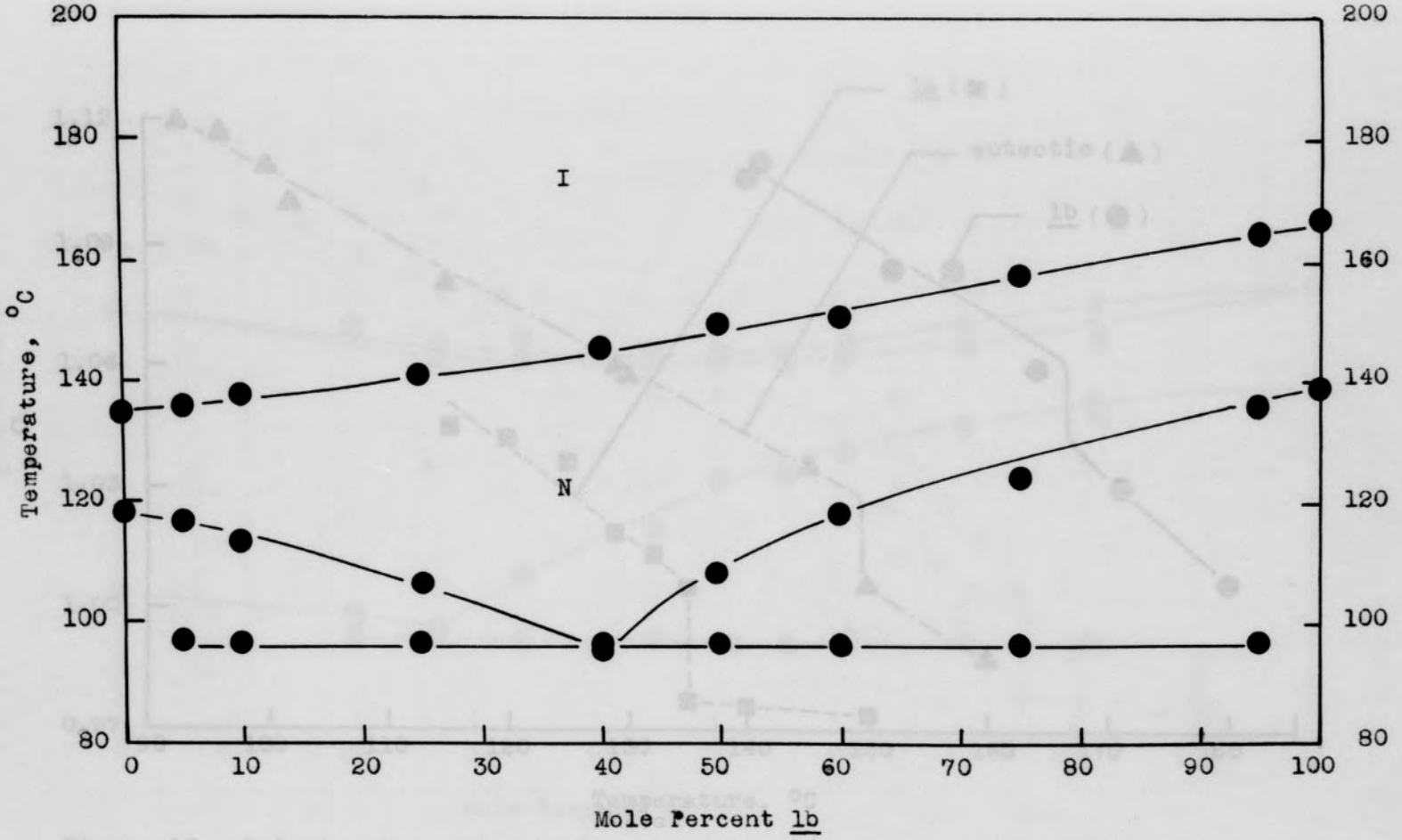


Figure 12. Phase Diagram of System 1a-1b (N = nematic, I = isotropic) [8]

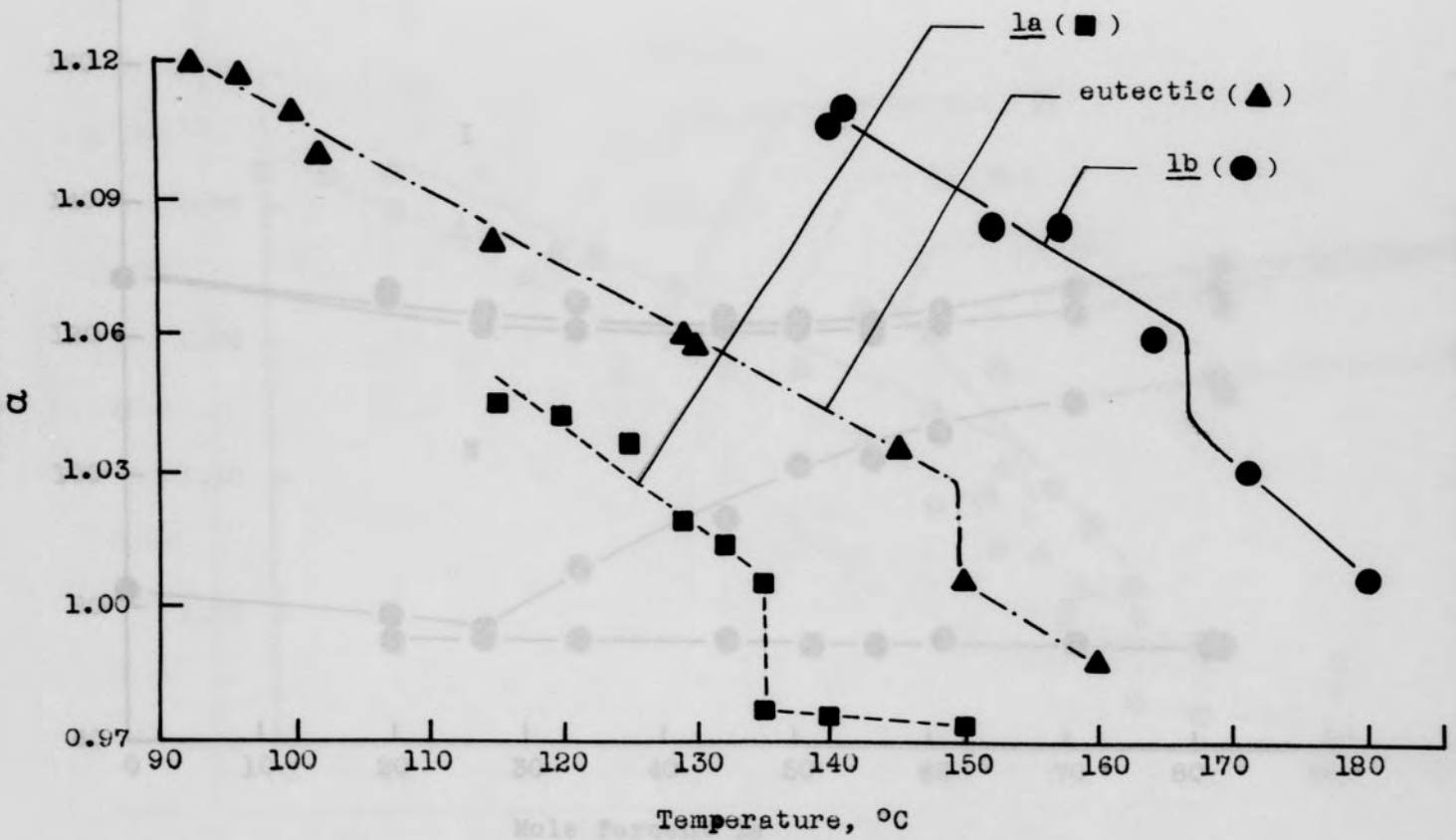


Figure 13. Relative Retention (α) of p-Xylene (m-Xylene = 1.00) on Stationary Liquid Phases of 1a, 1b, and Mixture of 1a-1b at Various Temperatures [8]

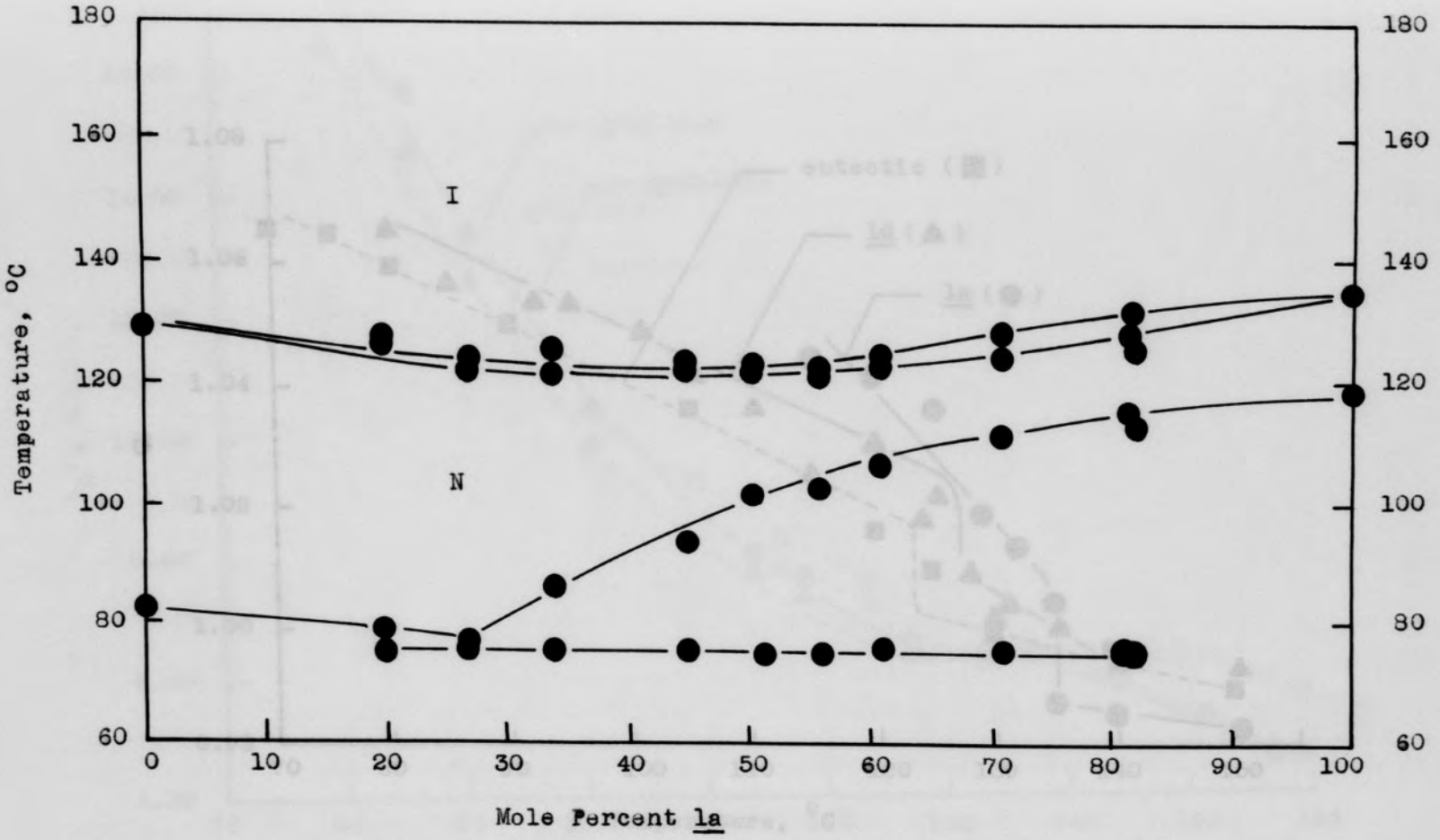


Figure 14. Phase Diagram of System la-ld (N = nematic, I = isotropic)[8]

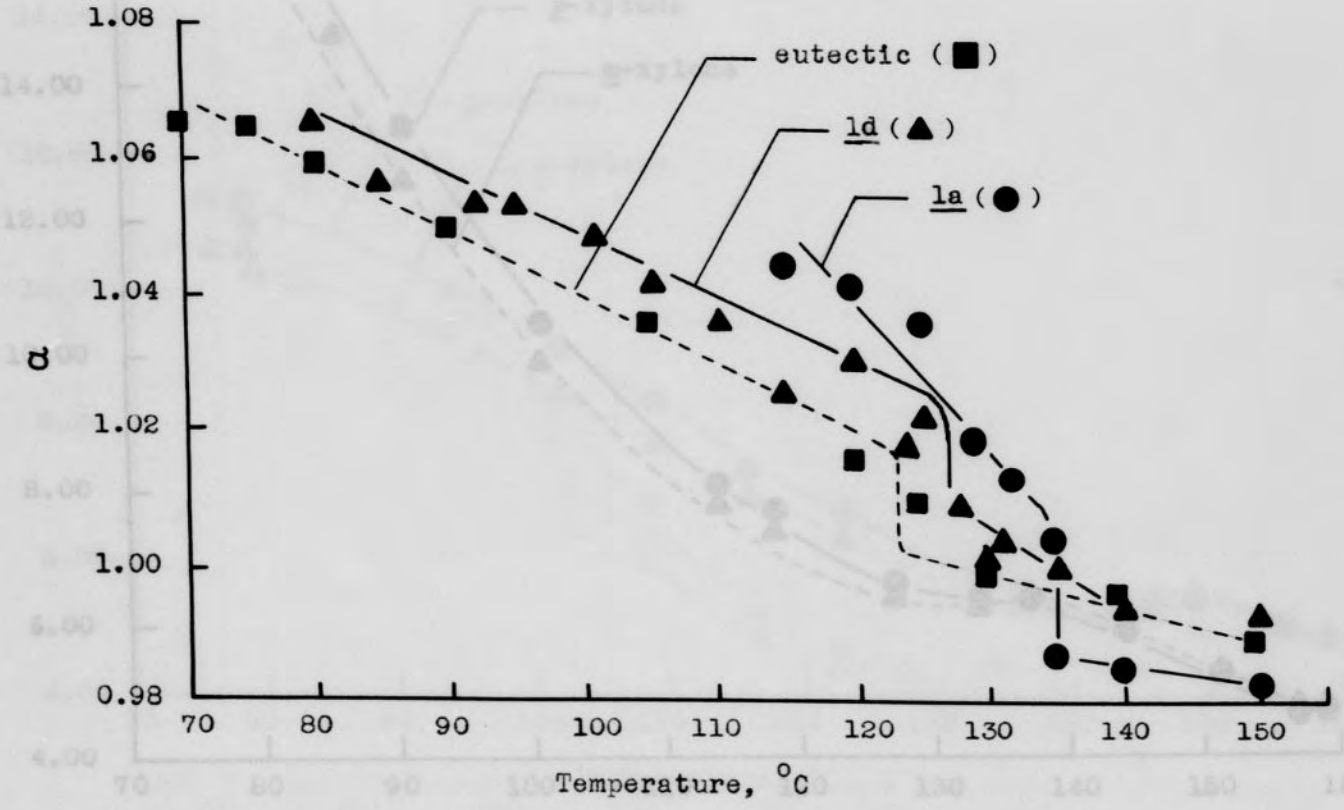


Figure 15. Relative Retention (α) of p-Xylene (m-Xylene = 1.00) on Stationary Liquid Phases of 1a, 1d, and Eutectic Mixture of 1a-1d at Various Temperatures

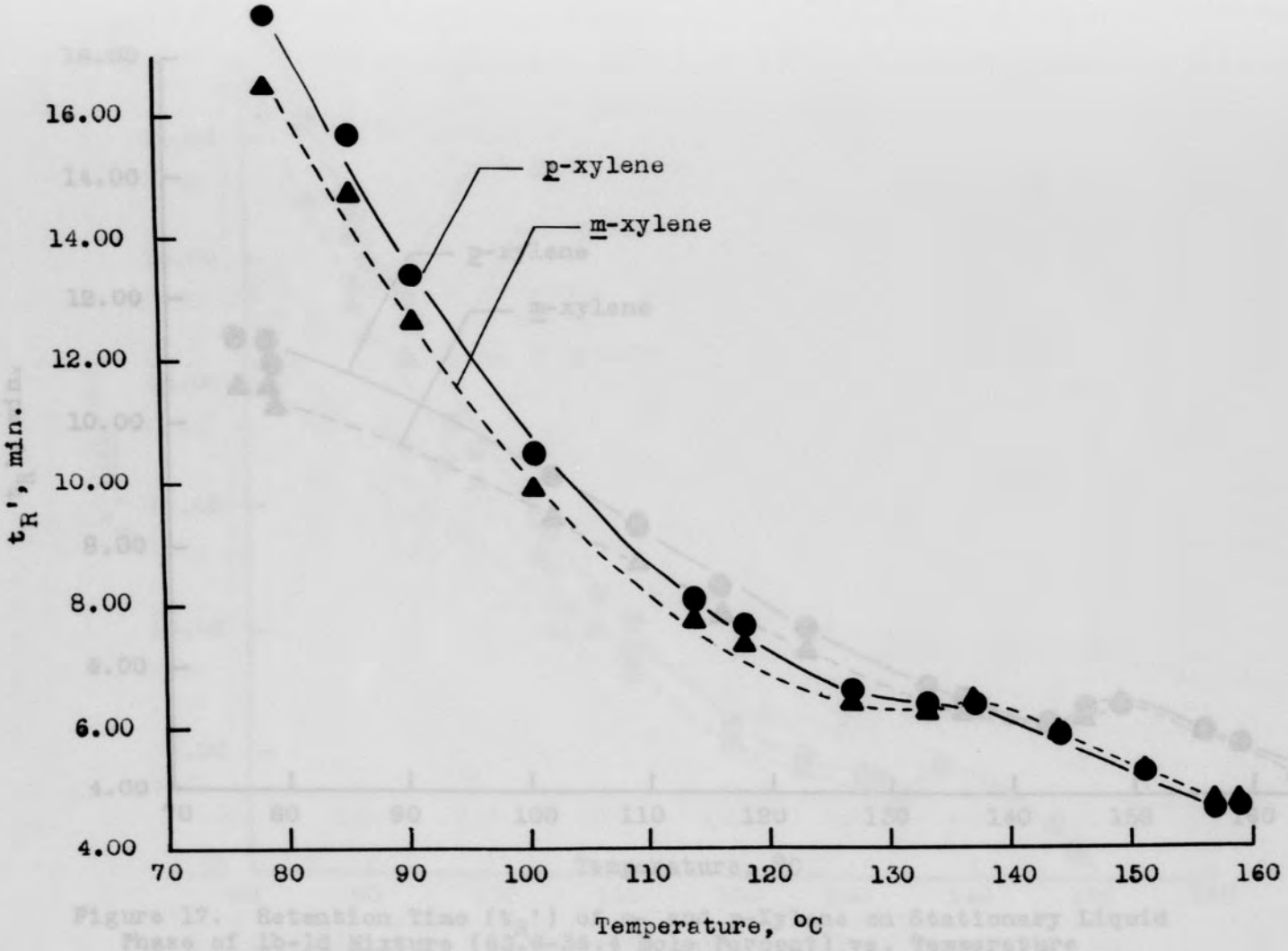


Figure 16. Retention Time (t_R') of m- and p-Xylene on Stationary Liquid Phase of 1b-1d Eutectic Mixture (22.2-77.8 Mole Percent) vs. Temperature

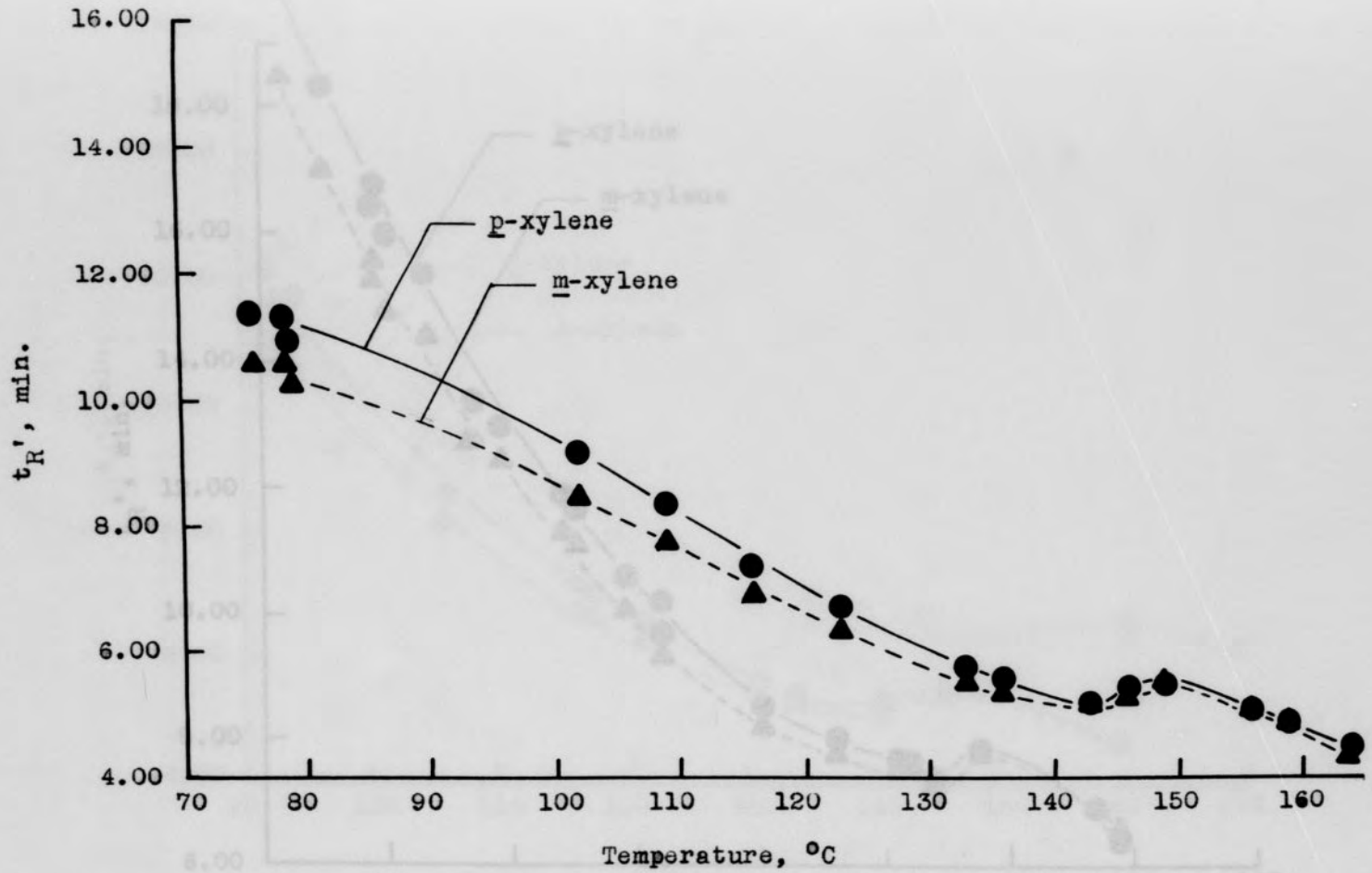


Figure 17. Retention Time (t_R') of m- and p-Xylene on Stationary Liquid Phase of 1b-1d Mixture (63.6-36.4 Mole Percent) vs. Temperature

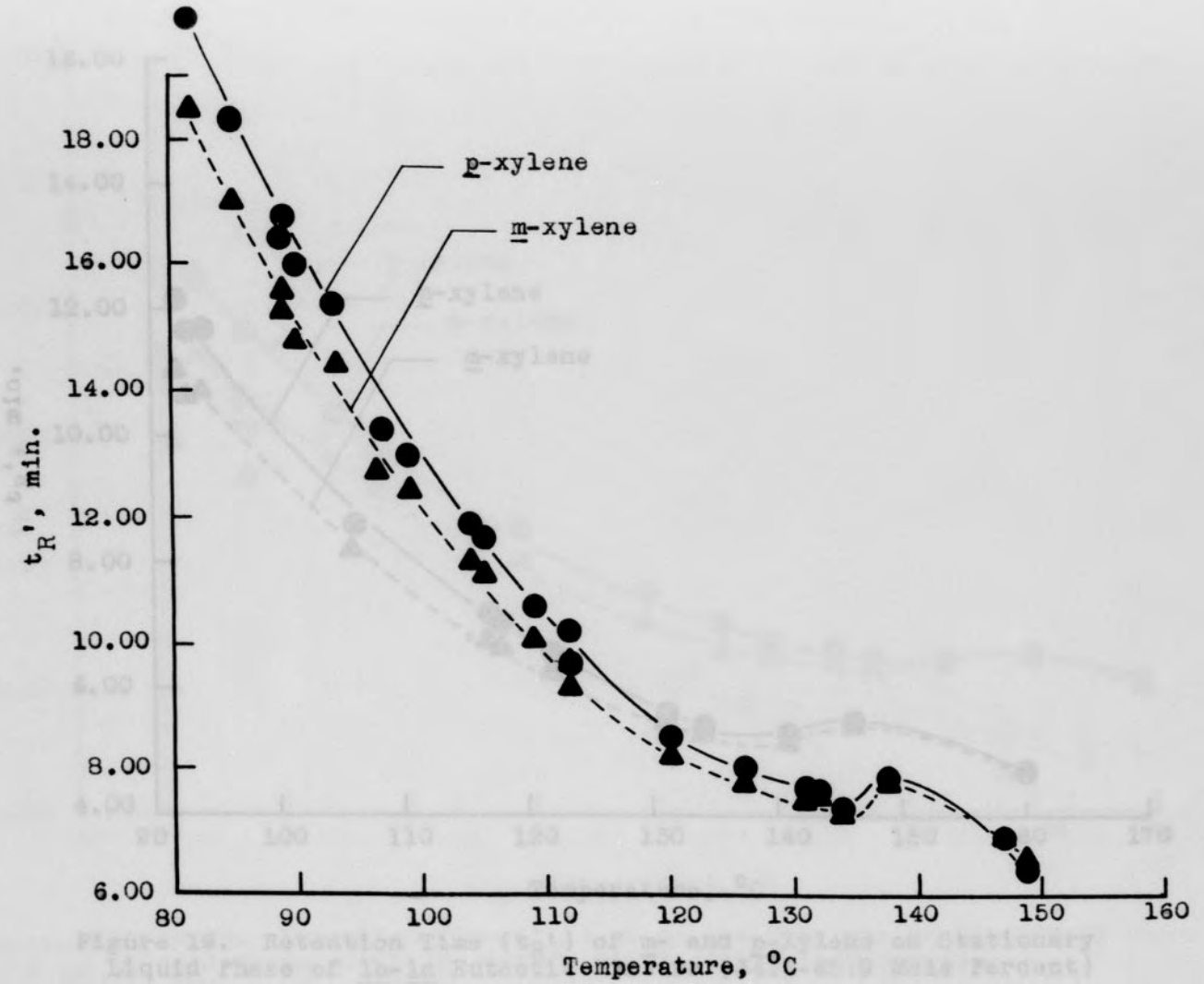


Figure 18. Retention Time (t_R') of m- and p-Xylene on Stationary Liquid Phase of 1a-1c Eutectic Mixture (36.0-64.0 Mole Percent) vs. Temperature

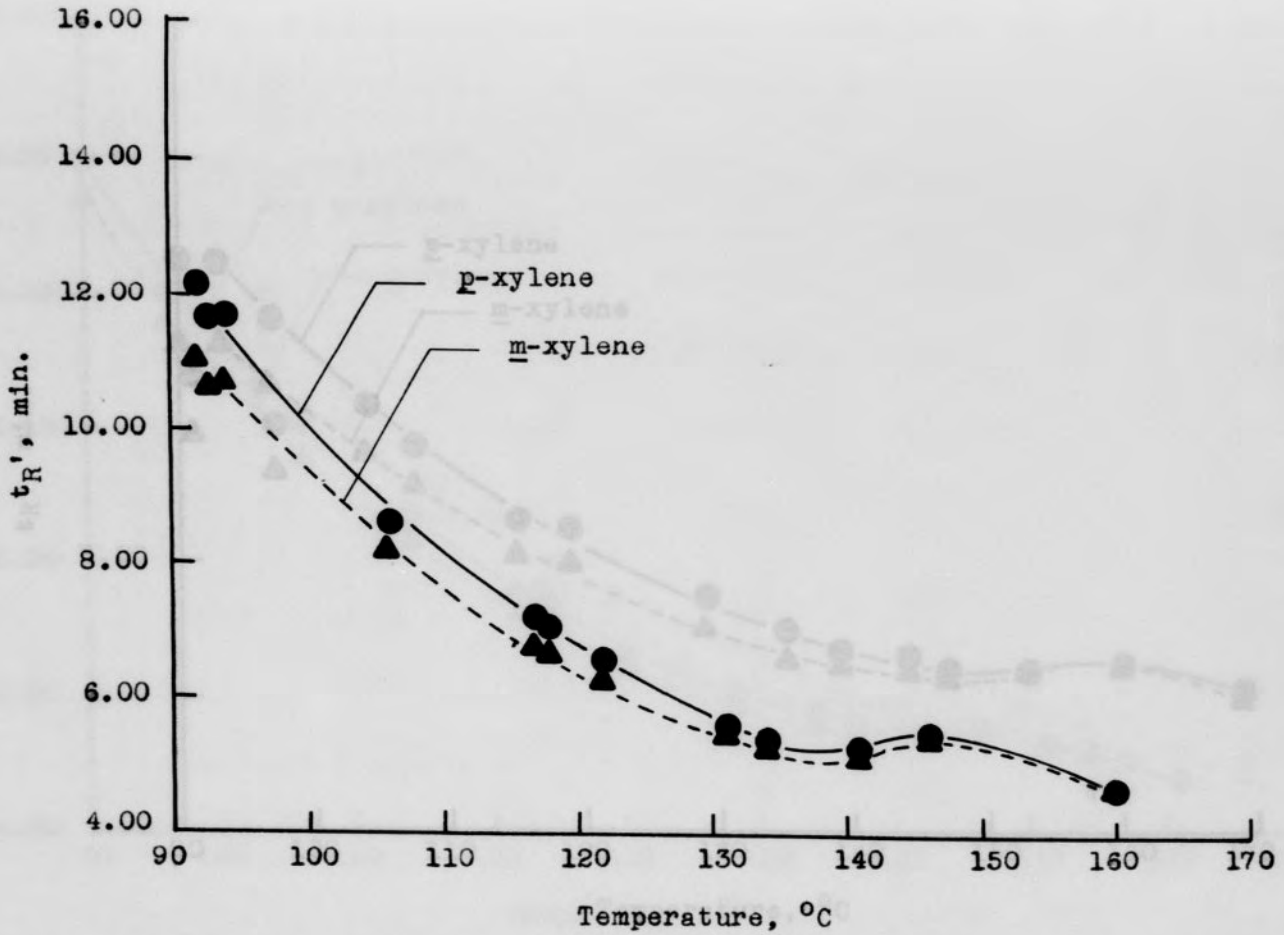


Figure 19. Retention Time (t_R') of m- and p-Xylene on Stationary Liquid Phase of 1b-1c Eutectic Mixture (34.1-65.9 Mole Percent) vs. Temperature

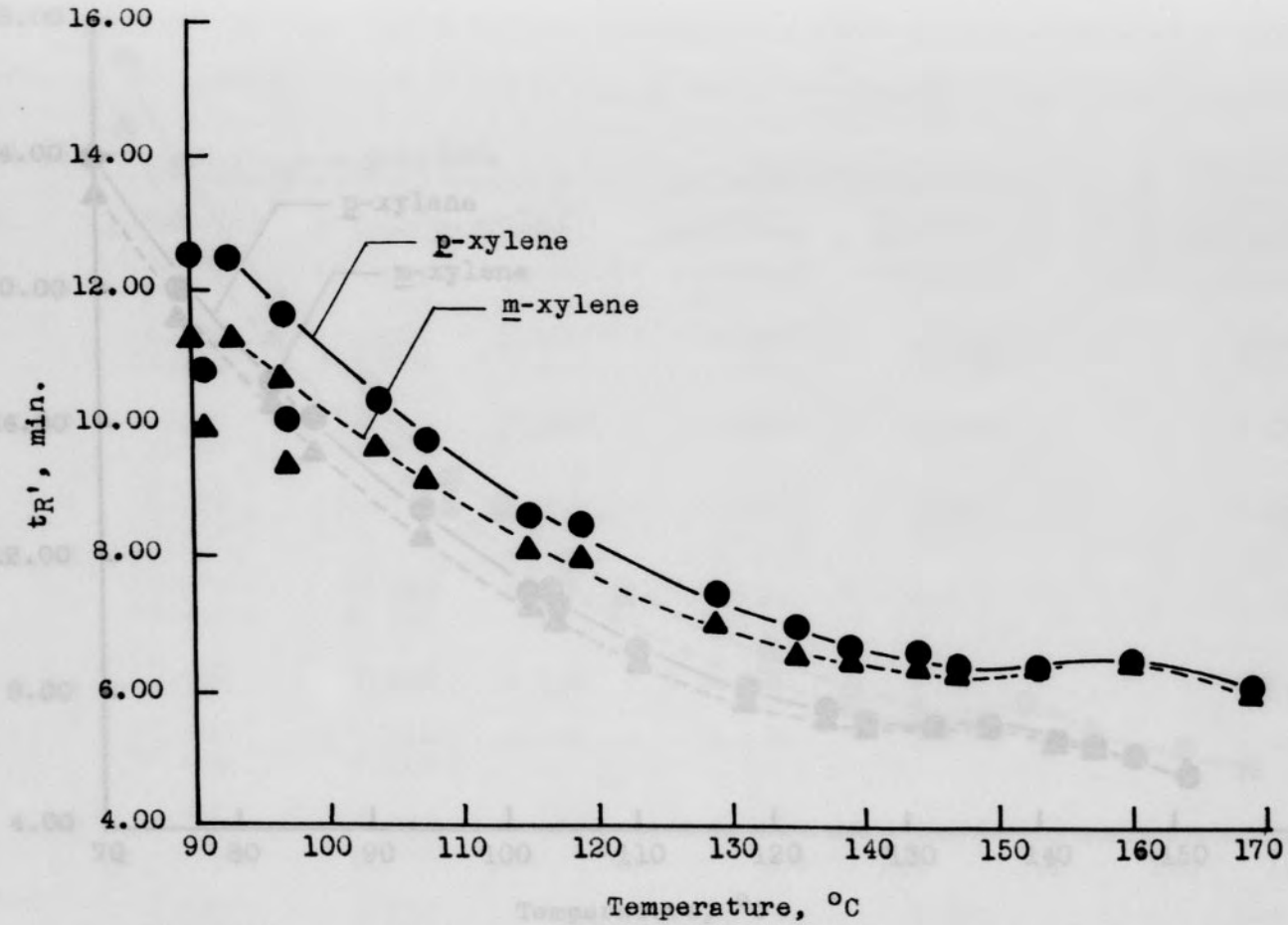


Figure 20. Retention Time (t_R') of m- and p-Xylene on Stationary Liquid Phase of 1b-1c Mixture (55.3-44.7 Mole Percent) vs. Temperature

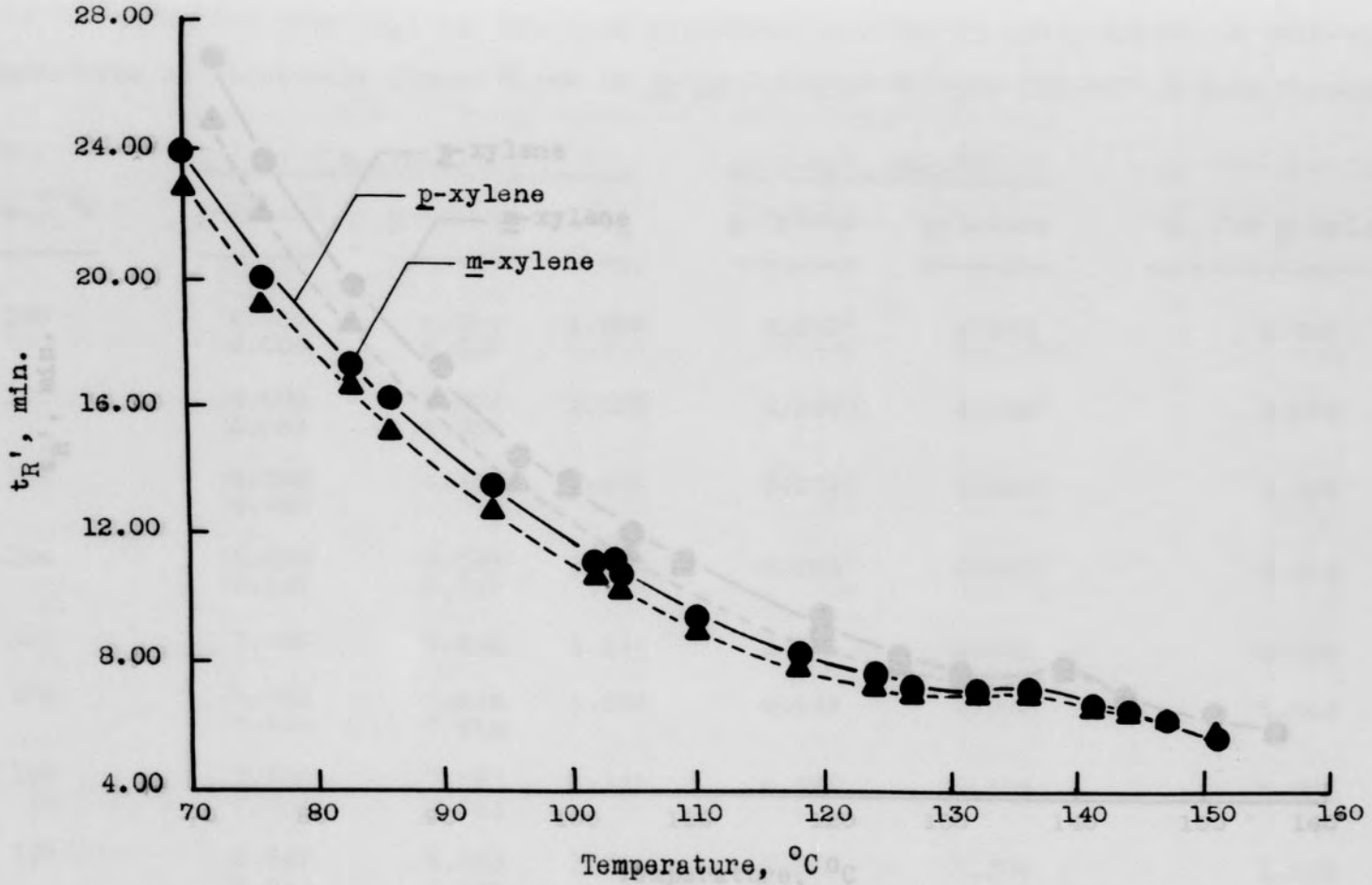


Figure 21. Retention Time (t_R') of m- and p-Xylene on Stationary Liquid Phase of lc-ld Eutectic Mixture (47.9-52.1 Mole Percent) vs. Temperature

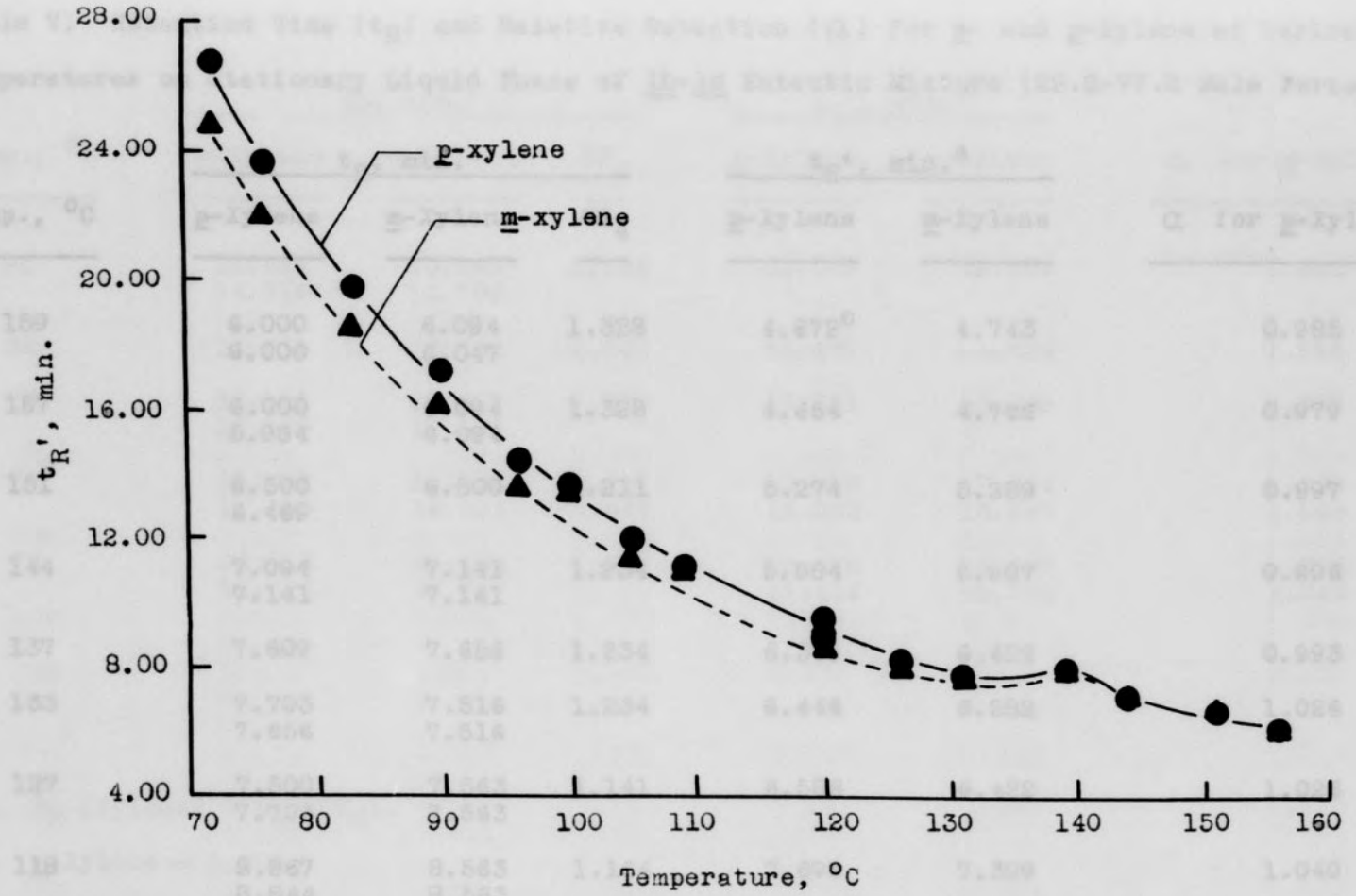


Figure 22. Retention Time (t_R') of m- and p-Xylene on Stationary Liquid Phase of 1c-1d Mixture (54.8-45.2 Mole Percent) vs. Temperature

Table V. Retention Time (t_R) and Relative Retention (α) for m- and p-Xylene at Various Temperatures on Stationary Liquid Phase of 1b-1d Eutectic Mixture (22.2-77.8 Mole Percent)

	t_R, min.			t_R', min.[a]		
Temp., °C	p-Xylene	m-Xylene	CH_4	p-Xylene	m-Xylene	α for p-Xylene[b]
159	6.000 6.000	6.094 6.047	1.328	4.672[c]	4.743	0.985
157	6.000 5.984	6.094 6.094	1.328	4.664	4.766	0.979
151	6.500 6.469	6.500	1.211	5.274	5.289	0.997
144	7.094 7.141	7.141 7.141	1.234	5.884	5.907	0.996
137	7.609	7.656	1.234	6.375	6.422	0.993
133	7.703 7.656	7.516 7.516	1.234	6.446	6.282	1.026
127	7.500 7.703	7.563 7.563	1.141	6.586	6.422	1.026
118	8.867 8.844	8.563 8.563	1.164	7.692	7.399	1.040
114	9.234	8.938	1.141	8.093	7.797	1.038
101	11.656 11.656	11.000 11.094	1.141	10.515	9.916	1.060

Table V. (Continued)

Temp., °C	t_R, min.			t_R', min.[a]		α for p-Xylene[b]
	p-Xylene	m-Xylene	CH_4	p-Xylene	m-Xylene	
91	14.428	13.703	1.094	13.378	12.609	1.061
	14.516	13.703				
86	16.675	13.703	1.047	15.677	14.726	1.065
79	18.891	17.609	1.070	17.751	16.539	1.070
	18.750	17.609				
76[d]	19.469	18.281	1.047	18.422	17.234	1.069
	17.070	16.094	1.047	16.023	15.047	1.065
72	20.516	19.234	1.047	19.469	18.187	1.070
	18.563	17.797		17.516	16.750	1.046

a. t_R (Xylene) - t_R (CH_4).

b. m-Xylene = 1.000.

c. Average for two runs.

d. Crystallization has begun.

Table VI. Retention Time (t_R) and Relative Retention (α) for m- and p-Xylene at Various Temperatures on Stationary Liquid Phase of 1b-1d Mixture (63.3-36.4 Mole Percent)

	t_R, min.			t_R', min.[a]		
Temp., °C	p-Xylene	m-Xylene	CH_4	p-Xylene	m-Xylene	α for p-Xylene[b]
164	5.891	5.891 5.844	1.422	4.469	4.446[c]	1.005
159	6.234	6.234	1.328	4.906	4.906	1.000
156	6.422 6.375	6.328 6.328	1.328	5.071	5.000	1.014
149	6.797 6.797	6.797 6.750	1.281	5.516	5.493	1.004
146	6.797	6.656	1.328	5.469	5.328	1.026
143	6.516 6.544	6.375 6.422	1.281	5.249	5.118	1.026
136	6.891	6.609	1.281	5.610	5.328	1.053
134	7.094 7.094	6.891 6.844	1.281	5.813	5.587	1.040
123	8.047 8.047	7.659 7.703	1.281	6.766	6.399	1.057
116	8.656	8.188	1.234	7.422	6.954	1.067

Table VI. (Continued)

Temp., °C	t_R, min.			t_R', min.[a]		α for p-Xylene[b]
	p-Xylene	m-Xylene	CH_4	p-Xylene	m-Xylene	
109	9.609 9.609	8.984	1.188	8.421	7.796	1.080
102	10.375	9.703	1.188	9.187	8.515	1.079
98	9.281	8.563	1.188	8.093	7.375	1.097
96[d]	10.094 9.844	9.469 9.094	1.141	8.953 8.703	8.328 8.093	1.075 1.075
94	9.656	9.094	1.164	8.492	7.930	1.071
93	9.586 9.563	9.020 9.000	1.094	8.481	7.916	1.071
91	10.281 10.047	9.703 9.469	1.141	9.140 8.906	8.562 8.328	1.068 1.069
89	10.047 10.000	9.469 9.422	1.141	8.888	8.305	1.070
79	12.094 12.000	11.375 11.281	1.094	11.000 10.906	10.281 10.187	1.070 1.071
78.5	12.516	11.750	1.094	11.422	10.656	1.072
76	12.469	11.703	1.094	11.375	10.609	1.072

a. t_R (Xylene) - t_R (CH_4).

b. m-Xylene = 1.000.

c. Average of two runs.

d. Crystallization has begun.

Table VII. Retention Time (t_R) and Relative Retention (α) for m- and p-Xylene at Various Temperatures on Stationary Liquid Phase of la-lc Eutectic Mixture (36.0-64.0 Mole Percent)

	t_R, min.			t_R', min.[a]		
Temp., °C	p-Xylene	m-Xylene	CH_4	p-Xylene	m-Xylene	α for p-Xylene[b]
149	7.844 7.844	8.094 8.094	1.422	6.422[c]	6.672	0.963
147	8.281	8.281	1.375	6.906	6.906	1.000
138	9.378 9.188	9.234 9.188	1.375	7.908	7.836	1.009
134	8.797 8.797	8.703 8.703	1.375	7.422	7.328	1.013
132	8.984 9.094	8.891 9.000	1.328	7.656 7.766	7.563 7.692	1.012 1.012
131	9.094 9.094	8.891 8.891	1.328	7.766	7.563	1.027
126	9.375 9.328	9.188	1.328	8.047	7.860	1.024
120	9.891 9.867	9.516 9.563	1.328	8.551	8.212	1.041
112	11.047 11.047	10.656 10.609	1.281	9.766	9.352	1.044

Table VII. (Continued)

Temp., °C	t_R, min.			t_R', min.[a]		α for p-Xylene[b]
	p-Xylene	m-Xylene	CH_4	p-Xylene	m-Xylene	
112	11.469	11.047	1.258	10.211	9.789	1.044
109	11.844 11.938	11.375 11.281	1.234	10.657	10.094	1.056
105	12.891 12.938	12.281 12.328	1.234	11.686	11.071	1.056
104	13.188	12.516	1.234	11.931	11.282	1.058
99	14.210 14.281	13.500 13.609	1.234	13.047	12.375	1.054
97	14.703 14.656	13.938 13.891	1.234	13.446	12.681	1.060
93	16.656 16.656	15.656 15.703	1.234	15.422	14.446	1.068
90	17.234	16.117	1.234	16.000	14.883	1.075
89	17.234 17.656	16.653 16.563	1.234	16.422	15.329	1.071
89	18.094 17.938 18.000	16.938 16.797 16.844	1.188	16.906 16.750 16.812	15.750 15.609 15.656	1.073 1.073 1.074

Table VII. (Continued)

Temp., °C	t_R, min.			t_R', min.[a]		α for p-Xylene[b]
	p-Xylene	m-Xylene	CH_4	p-Xylene	m-Xylene	
85	19.547	18.250	1.188	18.359	17.062	1.076
	19.469	18.188		18.281	17.000	1.075
80[d]	21.000	19.516	1.164	19.836	18.352	1.081
	20.141	18.703		18.977	17.539	1.082

a. t_R (Xylene) - t_R (CH_4).

b. m-Xylene = 1.000.

c. Average of two runs.

d. Crystallization has begun.

Table VIII. Retention Time (t_R) and Relative Retention (α) for m- and p-Xylene at Various Temperatures on Stationary Liquid Phase of 1b-1c Eutectic Mixture (34.1-65.9 Mole Percent)

Temp., °C	t_R, min.			t_R', min.[a]		
	p-Xylene	m-Xylene	CH_4	p-Xylene	m-Xylene	α for p-Xylene[b]
160	6.141 6.141	6.141 6.141	1.422	4.719[c]	4.719	1.000
146	6.938 6.938	6.891 6.891	1.375	5.563	5.516	1.009
141	6.609 6.609	6.469 6.516	1.281	5.328	5.212	1.022
134	6.844 6.797	6.609 6.609	1.359	5.462	5.250	1.040
131	7.000 7.000	6.797 6.797	1.328	5.672	5.469	1.037
122	7.844 7.938	7.563	1.281	6.610	6.282	1.052
118	8.328 8.281	7.891 7.891	1.234	7.071	6.657	1.062
117	8.469	8.000	1.234	7.235	6.766	1.069
106	10.281 10.328	9.656 9.656	1.328	8.677	8.228	1.055

Table VIII. (Continued)

Temp., °C	t_R, min.			t_R', min.[a]		α for p-Xylene[b]
	p-Xylene	m-Xylene	CH_4	p-Xylene	m-Xylene	
94	13.047	12.000	1.234	11.782	10.723	1.099
	12.984	11.914				
93	12.891	11.844	1.188	11.703	10.656	1.098
92	13.375	12.188	1.141	12.187	11.047	1.103
88[d]	14.609	13.563	1.188	13.421	12.093	1.110
	14.395	13.141		13.207	11.953	1.105
87[d]	15.047	13.656	1.141	13.875	12.469	1.113
	14.984	13.563		13.207	11.953	1.105
82[d]	14.773	13.375	1.141	13.632	12.234	1.114
	14.656	13.281		13.515	12.140	1.113
	14.500	13.141		13.359	12.000	1.113

a. t_R (Xylene) - t_R (CH_4).

b. m-Xylene = 1.000.

c. Average of two runs.

d. Crystallization has begun.

Table IX. Retention Time (t_R) and Relative Retention (α) for m- and p-Xylene at Various Temperatures on Stationary Liquid Phase of 1b-1c Mixture (55.3-44.7 Mole Percent)

	t_R, min.			t_R', min.[a]		
Temp., °C	p-Xylene	m-Xylene	CH_4	p-Xylene	m-Xylene	α for p-Xylene[b]
169	5.422	5.375	1.375	4.067	4.000	1.012
160	5.938	5.891	1.375	4.563	4.516	1.010
153	5.750 5.750	5.750 5.750	1.328	4.422[c]	4.422	1.000
147	5.750	5.609	1.328	4.422	4.281	1.031
144	5.938 5.938	5.750 5.703	1.328	4.610	4.399	1.048
139	6.047 6.047	5.797 5.844	1.328	4.719	4.493	1.050
135	6.281 6.281	5.891 5.894	1.281	5.000	4.612	1.084
129	6.750 6.844	6.422 6.422	1.282	5.516	5.141	1.073
118	7.797 7.750	7.281 7.234	1.281	6.493	5.977	1.086
115	7.891 7.891	7.328 7.375	1.234	6.657	6.118	1.088

Table IX. (Continued)

Temp., °C	t_R, min.			$t_{R'}$, min.[a]		α for p-Xylene[b]
	p-Xylene	m-Xylene	CH_4	p-Xylene	m-Xylene	
108	8.938	8.422	1.234	7.759	7.188	1.079
104	9.563	8.844	1.188	8.375	7.656	1.094
97	9.328	8.656	1.234	8.094	7.422	1.091
97	10.038 10.797	9.891 9.844	1.188	9.680	8.680	1.115
94	9.469		1.188	8.281		
93	11.750 11.609	10.469 10.516	1.188	10.492	9.305	1.128
91	9.891	8.984	1.141	8.859	7.977	1.116
90	11.750	10.516	1.234	10.516	9.282	1.133
89	10.000	9.141	1.141	8.859	7.977	1.111
85[d]	8.422	6.984	1.141	7.281	5.843	1.241

a. t_R (Xylene) - t_R (CH_4).

b. m-Xylene = 1.000.

c. Average of two runs.

d. Crystallization has begun.

Table X. Retention Time (t_R) and Relative Retention (α) for m- and p-Xylene at Various Temperatures on Stationary Liquid Phase of lc-ld Eutectic Mixture (47.9-52.1 Mole Percent)

	t_R, min.			t_R', min.[a]		
Temp., °C	p-Xylene	m-Xylene	CH_4	p-Xylene	m-Xylene	α for p-Xylene[b]
151	6.938 6.984	7.000 6.984	1.328	5.633[c]	5.664	0.995
147	7.516 7.563	7.563 7.563	1.328	6.212	6.235	0.996
144	7.797 7.797	7.797 7.609	1.328	6.469 6.469	6.469 6.281	1.000 1.029
141	8.000 7.984	7.984 7.938	1.281	6.711	6.680	1.005
136	8.516 8.516	8.469 8.398	1.281	7.235	7.153	1.011
132	8.328 8.328	8.234 8.234	1.234	7.094	7.000	1.013
127	8.469 8.469	8.328 8.328	1.281	7.188	7.047	1.020
124	8.797 8.797	8.516 8.516	1.234	7.563	7.282	1.039
118	9.422 9.422	9.234 9.141	1.234	8.188	7.954	1.029

Table X. (Continued)

Temp., °C	t_R, min.			t_R', min.[a]		α for p-Xylene[b]
	p-Xylene	m-Xylene	CH_4	p-Xylene	m-Xylene	
110	10.500	10.141	1.188	9.300	8.953	1.039
104	11.797	11.281	1.234	10.563	10.047	1.042[c]
	11.984	11.046		10.750	10.235	
103	12.047	11.516	1.234	10.813	10.282	1.052
102	12.281	11.797	1.188	11.093	10.609	1.045
	12.281	11.750	1.141	11.140	10.609	1.050
94	14.609	13.844	1.188	13.421	12.656	1.060
	14.609	13.844				
86	17.375	16.375	1.141	16.234	15.234	1.066
	17.328	16.328		16.187	15.187	
83	18.469	17.830	1.141	17.328	16.689	1.038
76	21.656	20.281	1.141	20.515	19.140	1.072
70	25.750	24.000	1.094	24.056	22.906	1.050
	25.703	24.000		24.009	22.906	1.048
64[d]	16.000	14.609	1.094	14.906	13.515	1.103
	17.750	16.375		16.656	15.281	1.090

a. t_R (Xylene) - t_R (CH_4).

b. m-Xylene = 1.000.

c. Average of two runs.

d. Crystallization has begun.

Table XI. Retention Time (t_R) and Relative Retention (α) for m- and p-Xylene at Various Temperatures on Stationary Phase of lc-ld Mixture (54.8-45.2 Mole Percent)

	t_R, min.			t_R', min.[a]		
Temp., °C	p-Xylene	m-Xylene	CH_4	p-Xylene	m-Xylene	α for p-Xylene[b]
156	7.609 7.609	7.609 7.609	1.422	6.187[c]	6.187	1.000
151	8.141 8.188	8.234 8.188	1.422	6.743	6.789	0.993
144	8.656 8.609	8.656 8.656	1.422	7.211	7.234	0.997
139	9.516 9.563	9.422 9.422	1.422	8.118	8.000	1.015
131	9.281	9.094	1.375	7.906	7.719	1.024
126	9.750 9.797	9.516 9.563	1.375	8.397	8.165	1.028
120	10.984 11.047	10.797 10.797	1.375	9.641	9.422	1.023
120	10.469	10.094	1.375	9.094	8.719	1.043
109	12.563 12.563	12.234 12.281	1.328	11.235	10.930	1.028
105	13.375	12.750	1.328	12.047	11.422	1.055

Table XI. (Continued)

Temp., °C	t_R, min.			t_R', min.[a]		α for p-Xylene[b]
	p-Xylene	m-Xylene	CH_4	p-Xylene	m-Xylene	
100	15.000 15.150	14.891	1.328	13.747	13.563	1.014
96	15.750	14.938	1.281	14.469	13.657	1.059
90	18.499 18.516	17.452 17.468	1.234	17.274	16.226	1.065
83	21.094	19.844	1.234	19.860	18.610	1.067
76	24.891	23.281	1.211	23.680	22.070	1.073
72	27.984	26.094	1.188	26.796	24.906	1.076

a. t_R (Xylene) - t_R (CH_4).

b. m-Xylene = 1.000.

c. Average for two runs.

Table XII. Melting and Nematic-Isotropic Transition Ranges for Various Compositions of 1b-1d Mixtures

Sample Number	Composition, Mole % 1b	Melting Range, °C	Nematic-Isotropic Transition Range, °C
15	10.3	76-81	129-129.5
I	24.5	76.5-78.5	131-131.5
14	33.1	76-104	
IV	40.0	76-122	135-139.5
II	49.8	76-124.5	135-144
13	52.6		
VII	60.7	76-131.5	141-148.5
VIII	70.2	76-130.5	143.5-153
10	82.9	76.5-130.5	152-158
9	89.9		158-164.5

Table XIII. Melting and Nematic-Isotropic Transition Ranges for Various Compositions of la-lc Mixtures

Sample Number	Composition, Mole % la	Melting Range, °C	Nematic-Isotropic Transition Range, °C
0-7	14.2	84-100.5	132.5-133.5
0-1	25.1	84-98.5	131-133.5
0-3	36.0	84-85.5	130-130.5
0-2	45.9	85-96	128.5-129
0-5	64.1	84-111	128-130
0-4	79.0	84-111.5	129.5-130.5
0-6	89.8	84-117	131.5-133

Table XIV. Melting and Nematic-Isotropic Transition Ranges for Various Compositions of 1b-1c Mixtures

Sample Number	Composition, Mole % 1b	Melting Range, °C	Nematic-Isotropic Transition Range, °C
N-7	10.0	85-103.5	136.5-137.5
N-1	26.2	85.5-94	140-141.5
N-4	35.0	86-88	143-144
N-8	44.7	86-105	145-146.5
B	51.0		146.5-148.5
N-2	51.8	86-114.5	
A	60.4		150-153.5
N-5	63.7	86.5-124.5	152-157
C	69.7		154-158.5
N-3	75.4	86	155.5-159.5
N-6	83.9	86-132.5	158.5-161
N-11	90.1	86-127	160-162.5

Table XV. Melting and Nematic-Isotropic Transition Ranges for Various Compositions of lc-ld Mixtures

Sample Number	Composition, Mole % lc	Melting Range, °C	Nematic-Isotropic Transition Range, °C
M-12	10.3	68-79	129-130
M-1	24.9	67-78	127.5-129.5
M-4	34.75	67-72	129.5-130.5
M-2	48.2	67-69	129.5-130.5
M-7	55.4	67.5-76	130.5-131
M-5	64.5	67.5-90	131.5-132.5
M-3	74.5		131.5-133
M-10	83.6	67-100	133-134
M-8	83.7	67-91	133-133.5
M-6	85.9		132-133.5
M-11	86.2		133.5-134
M-9	95.9		134.5-136